THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 26 OCTOBER, 1941 No. 10

PYROXENES OF COMMON MAFIC MAGMAS. PART 2.

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HYPOTHESES ON THE TREND OF CRYSTALLIZATION OF PYROXENES IN BASALTS

The writer has extracted and herewith presents what he considers to be the kernel of thought in each of several papers dealing with the crystallization of pyroxenes from basalts. Many of the concepts in these papers are built upon primary data presented in Wahl's classic paper (1907) "Die Enstatitaugite" and various general papers by J. H. L. Vogt. A number of other less fundamental articles dealing with pyroxenes in basalts might have been included but those quoted seemed sufficient to give the trend of ideas on the problem at hand.

Asklund (1925)

Asklund calculated the MgO-CaO-FeO proportions of all superior analyses of diabases, gabbros, norites and pyroxenites in Washington's Tables. By referring to the original articles on these rocks he noted, whenever possible, whether one or two pyroxenes were present in the rock.

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* Due to the temporary absence of the author from the country the article was not proof read by Dr. Hess.

Upon plotting the points for rocks with one and two pyroxenes he found an area in which two pyroxenes were characteristic and outside of which only one pyroxene was the rule (Fig. 5). From this he concluded that despite the suggestion from Bowen's laboratory investigation of clinoenstatite-diopside relations, (which showed complete solid solution with a minimum), natural occurrences indicated limited miscibility between calcium-poor and calcium-rich magnesian pyroxenes. This is the major contribution of the paper. There follows a considerable discussion of the chemistry of crystallization of pyroxenes. In the present writer's opinion this is of little value since it is based on certain unacceptable tacit assumptions, the most important of which is that only the chemical composition of the rock is considered and not the probable magma from which the rock was derived. Nevertheless, the paper is of much importance since it marks the first step in the trend of thought to be followed by many subsequent papers and no doubt formed a basis for further exploration and served as a stimulus towards this end.

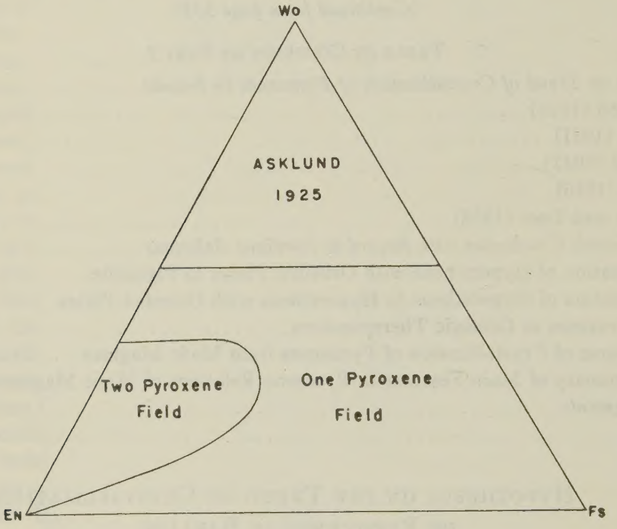

FIG. 5

Barth (*1931*)

Barth studied pyroxenes from basalts and took exception to Asklund's conclusion of partial miscibility of pyroxenes. The following quotation sums up Barth's conclusions: "Pigeonite is the most abundant pyroxene of volcanic rocks. Pyroxenes crystallizing from a basaltic magma exhibit a regular sequence of crystallization from diopsidic to hypersthenic, during which the content of $MgSiO_3$ may remain constant or increase slightly (see Fig. 6). . . . In agreement with the experimental studies of Bowen the present survey indicates a complete series of solid solutions in natural basaltic pyroxenes and consequently fails to demonstrate the discontinuity proposed by Asklund." Barth points out many fundamental details in pyroxene relations in the paper and has an ingenious method of attack on the problem which to some extent is followed by all later investigators.

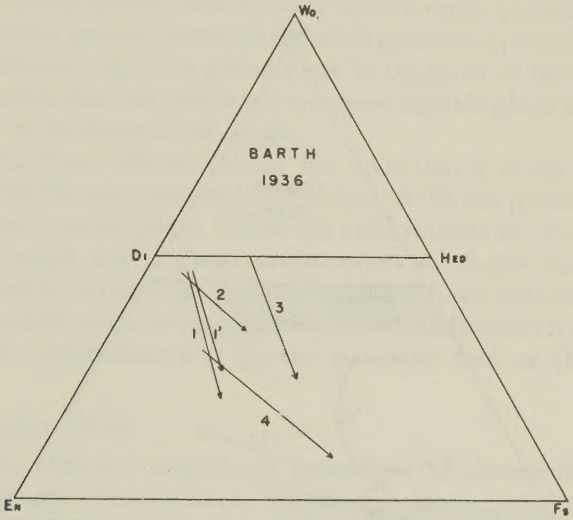

FIG. 6

His deduction as to the chemical composition of the groundmass pyroxene based on the normative Wo-En-Fs of the rock is open to question in that it assumes only one pyroxene is present.

Barth's views in a later paper (1936) are essentially the same, but stated even more forcibly. ". . . literally hundreds of typical basalts from all over the world show with remarkable uniformity the progressive change in the pyroxene phases from diposidic to clinohypersthenic, none but a very determined doubter could therefore fail to accept this as the *normal* course of crystallization of pyroxene from a basaltic lava."

Tsuboi (1932)

Tsuboi's skillful analysis of the trends of crystallization of pyroxenes from magmas, with particular examples from Japanese volcanic suites, shows that the views of Asklund and Barth are not incompatible, and goes more deeply into the chemical relations. The following quotation and Fig. 7 sum up his conclusions.

"In the intratelluric stage, either one of the monoclinic and rhombic pyroxenes starts the crystallization according to whether the composition of the original magma is in the field of monoclinic or of rhombic pyroxenes. As crystallization proceeds, the residual liquid changes its composition, following a course such as that indicated either by L_1 or by L_1'; and when the two-pyroxene boundary, CD, is reached the other one of the two pyroxenes joins in the crystallization. In the meantime the crystals of monoclinic and rhombic pyroxenes change their compositions respectively from diopsidic to hedenbergitic, and from enstatitic to hypersthenic, approximately as indicated by the arrows M and R. The hatched areas in the figure represent roughly the limits of miscibility of the pyroxenic components under the condition (designated as "condition A") that prevails in the intratelluric stage.

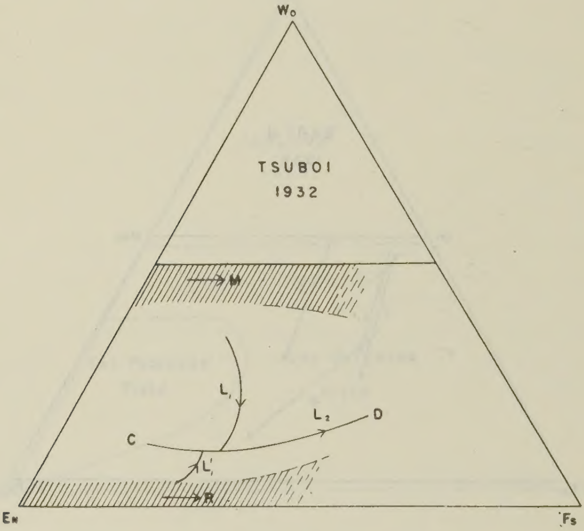

FIG. 7

"In the effusive stage, as the great majority of instances shows, another condition (designated as "condition B") prevails, under which there is no limit to the miscibility of the pyroxenes. Then the pyroxenic components of the residual liquid crystallize in a single pigeonitic phase, without splitting into two pyroxenes. In exceptional cases, however, condition A seems to prevail even in the effusive stage.

"The outstanding feature of my theory is in the assumptions that (i) the pyroxenic components are only partially miscible in the intratelluric stage, while (ii) they are completely miscible in the effusive stage (with rare exceptions)."

Kuno (*1936*)

The writer considers Kuno's papers to be among the finest examples in the literature of careful, accurate, and intelligent petrographic work. It is because of this quality that Kuno is able to make an important addition to Tsuboi's general theory of trends of pyroxene crystallization.

Kuno observes pigeonite phenocrysts in the lavas of the Hakone volcano and concludes that they must represent a stable phase under certain conditions in the intratelluric stage.

In general Kuno follows Tsuboi, but adds that if in the intratelluric stage the Mg:Fe molecular ratio is less than 45:55, one pyroxene (pigeonite) becomes a stable phase. Where the ratio exceeds 45:55 a two-pyroxene field (augite and orthopyroxene) exists as Tsuboi stated. In the effusive stage Kuno believes that pigeonite will form metastably because of rapid crystallization as suggested by Bowen and Schairer, regardless of whether the composition is in the two pyroxene field or the pigeonite field.

Wager and Deer (*1939*)

Wager and Deer in a magnificent memoir on the Skaergaard intrusion, made a thorough investigation of the clinopyroxenes, including a number of chemical analyses. It was thus possible to extend the curve for crystallization of the clinopyroxene of basaltic magmas from the early stages, as given by Kuno and Kennedy, to the very latest stage with extreme differentiation; at which stage they are practically pure Ca-Fe pyroxenes (Fig. 8). A study of the orthopyroxenes shows that they accompany the clinopyroxene up to that point where the Mg:Fe molecular ratio becomes approximately 35:65 They thus shift Kuno's limit for the intratelluric two-pyroxene field 10 per cent farther towards the iron-rich side of the diagram.

In the present paper the iron-rich clinopyroxenes of the Skaergaard would be called *ferroaugites*. Wager and Deer following more or less accepted usage called them *pigeonites*. To do so, however, completely confuses the genetic relations between the pyroxenes as was shown elsewhere in this paper. These ferroaugites are not the same phase as the typical pigeonites of the groundmass of basalts with 2V near 0°. Thus Wager's and Deer's discussion of the trend of crystallization of the pyroxenes, based on this unacceptable assumption, is considered invalid. This is not meant to be an unfavorable reflection on the work of Wager and Deer, for which the present writer has a very high regard. From the data they had, the conclusions they drew follow logically. It is rather a commentary on the confusion which may result from the lack of an adequate nomenclature for pyroxenes and the failure of the science as a whole to make precise distinctions between even the commonest varieties of clinopyroxenes.

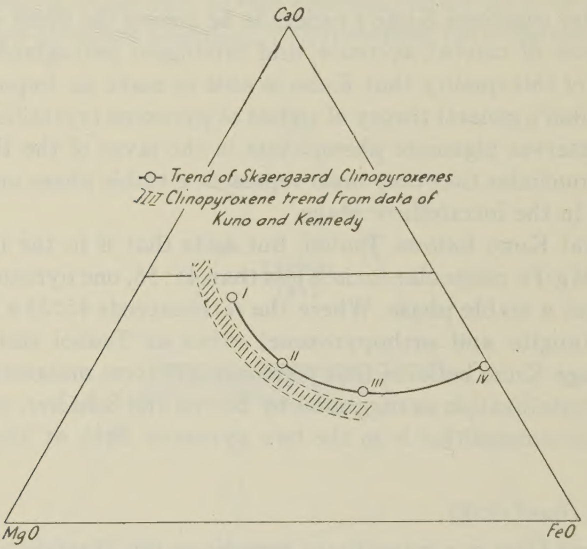

FIG. 8

PRESENT WRITER'S CONCLUSION WITH REGARD TO PYROXENE RELATIONS

Before proceeding to a theory as to the course of crystallization of pyroxenes from common mafic magmas, it is desirable to bring together in the form of conclusions, and to some extent speculations, various observations concerning pyroxene relations set forth in the descriptive portion of this paper.

Very few chemical analyses of pigeonites have been made and it appears to the writer that only one of these is completely satisfactory. This one is the so-called "uniaxial augite" from Mull (Hallimond 1914). An analysis of the pyroxene from a meteorite (eucrite, Moore County, North Carolina, Henderson and Davis, 1936) probably represents accurately the chemical composition of the pigeonite found in the specimen, but has the disadvantage that part of it has apparently broken down, inverting to hypersthene with thin plates of augite. It is thought that this breakdown of the pigeonite would not involve any change in the bulk composition of the pyroxene. Bowen (1933) has estimated the composition of an iron-rich pigeonite from a slag.

TABLE 1

	1 Mull, Hallimond	2 N. C. Eucrite, Henderson and Davis	3 Bushveld, Hy inverted from Pigeonite	3a* Same as 3, subtract small amount impurity	4 Stillwater, Hy inverted from Pigeonite in hornfels	5 Slag, Bowen
SiO_2	49.72	49.37	51.67	51.40	50.24	
Al_2O_3	.90	1.55	1.80	1.78	4.52	
Fe_2O_3	1.72	1.83	1.40	1.40	.41	
FeO	27.77	26.44	20.57	20.68	21.81	
MgO	12.69	15.54	19.34	19.37	15.81	
CaO	3.80	4.60	4.45	4.07	4.39	
Na_2O	.23	—	.12	.11	.18	
K_2O	.12	—	—	—	.04	
H_2O+	1.27	—	.36	.37	1.42	
H_2O-	.08	—	.04	.04	.04	
TiO_2	.85	.62	.30	.30	.69	
MnO	.98	.37	.47	.48	.43	
Total	100.13	100.32	100.52	100.00	99.98	
Analyst	Hallimond	E. P. Henderson	R. B. Ellestad		R. B. Ellestad	
Molecular per cent	Wo 9	$9\frac{3}{4}$		$8\frac{1}{2}$	10	$8\frac{3}{4}$
	En 40	$45\frac{3}{4}$		57	$50\frac{1}{2}$	$12\frac{1}{4}$
	Fs 51	$44\frac{1}{2}$		$34\frac{1}{2}$	$39\frac{1}{2}$	79

* Impurity, a small amount of augite (2.5%). The augite from this specimen was also analyzed so the correction should be quite accurate. The analysis was recalculated to 100 per cent.

Other purported analyses of pigeonites are as follows: (1) Pigeon Point (Winchell, 1900), (2) Åland Islands (Wahl, 1907), (3) Lake Onega (Wahl, 1907), (4) Deccan trap (Washington, quoted by Fenner, 1929), (5) Hiva Oa (Barth (1931A) and (6) Hakone volcano (Kuno 1940). In the writer's opinion all six of these analyses represent mixtures of augite and pigeonite. Through the courtesy of F. F. Grout the writer obtained a thin section of the rock from which the analyzed "pigeonite" from Pigeon Point was separated. A. N. Winchell very kindly supplied the writer with some of the original pyroxene separate on which the analysis was made. Examination of the slide and pyroxene separate showed that purplish augite, ($2V=43°-47°$, $Z\wedge c=40°$) was present in considerable quantity in both. As pointed out previously pigeonite is always accompanied by augite in rocks. In specimens (2) to (6) the bulk pyroxene was analyzed and no attempt apparently was made to separate a pigeonite from an augite. In analyses (4), (5) and (6) a wide variation in optic angles was reported on the material analyzed, ranging from near 50° to 0°. This again, as previously pointed out, indicates that both augite and pigeonite are present. The material of analyses (2) and (3) are incompletely described and have the added disadvantage of being inferior analyses (summations over 101). In (6) Kuno notes many grains with $2V=44°-36°$ and another group with 2V near 0°.

In Table 1 the two analyses which the writer believes are representative of the mineral pigeonite are given and two analyses of hypersthene with augite plates, which the writer considers to be pigeonite inverted to orthopyroxene upon slow cooling. Note the uniformity of $CaSiO_3$ component shown in all of the analyses of Table 1.

A. Relation of Hypersthene with Oriented Plates to Pigeonite.

The mutually complementary relationship of hypersthene with oriented plates and pigeonite has already been discussed. Ordinary hypersthene of igneous rocks contains uniformly about four and a half molecular per cent of the Wo component in solid solution (probably as diopsidic pyroxene) (Hess and Phillips 1940). Hypersthene with oriented plates contains uniformly about nine per cent, or twice as much. This is the amount found in the reliable analyses of pigeonite (see Table 1). In the writer's opinion there is strong evidence to indicate that the hypersthene with oriented plates is pigeonite, which has by slow cooling inverted to orthopyroxene. The oriented plates represent the excess Wo above the four and a half per cent which is the maximum soluble in hypersthene and the excess separates from the orthopyroxene in the form of augite ($2V \doteqdot 50°$). An additional indication of the inversion is the arrangement of the plates themselves. Hypersthene does not normally occur as twinned crystals in igneous rocks. Pigeonites commonly form either a pair or multiple twins with the composition plane (100). The oriented plates in many hypersthene crystals which contain them are arranged in two sets—herring bone-like—or in multiple sets in such a way as to suggest that each set was developed in a twin of the original pigeonite (see Figs. 3 and 4).

The commonest orientation of the plates is such that they are parallel to the *b* crystallographic axis and make an angle of approximately 74° with the *c* axis. This would be near a (102) plane in the hypersthene crystal, but a (102) crystal face has not been reported for this mineral and it seems to be an unlikely plane for development of lamellae by exsolution. If, however, the plane were related to the crystallographic directions of an original pigeonite, it would then become (001). Pigeonites commonly have a well developed (001) parting so that the orientation of the lamellae strongly suggests that they were developed in original pigeonite, before or during inversion to hypersthene. Exsolution lamellae having this orientation were observed in the pigeonite of the Moore County, North Carolina, eucrite (meterorite).

From the petrological evidence the case is also strong. Hypersthene with oriented plates is characteristic of *slowly cooled* intrusives and pigeonite is absent in these. Pigeonite is characteristic of *rapidly cooled* extrusives and hypersthene with oriented plates is absent in them. Whereas the intermediate type, the fine grained intrusives, may show both forms. In those rare cases where pigeonite began to crystallize in depth and the magma containing it was suddenly extruded, pigeonite phenocrysts will be found as in Hakone volcano.

B. Relation of Hypersthene to Hypersthene with Oriented Plates.

In the Stillwater, Bushveld, Skaergaard, and the New Jersey diabases it was shown that where the MgO:FeO molecular ratio of calcium-poor pyroxene was greater than approximately 7:3, normal orthopyroxene was present. When the ratio was less than 7:3, either hypersthene with oriented plates or pigeonite was present, depending probably on the rate of cooling. In the other igneous rocks discussed, such as the Duluth gabbro, Hakone andesites, Whin Sill, etc., the same relationship holds but the data were not available as to the exact ratio at which the change occurred. The immediate cause for this relationship can be found in Bowen's and Schairer's MgO-FeO-SiO_2 paper. A curve for the temperature of inversion of pyroxenes of the clinoenstatite-clinoferrosilite series to the orthorhombic enstatite-ferrosilite series is given showing that this inversion takes place at about 1145°C. for the magnesian end of the series and decreases to about 970°C. for a pyroxene very near the iron-rich end of the series.* This inversion curve was determined by heating natural orthopyroxenes containing the usual small amount of Wo so that it is more directly applicable to the pyroxenes here under consideration than would be the pure En-Fs end-members. From this curve and the observed relations mentioned above, it can be concluded that for pyroxenes more magnesian than $En_{70\pm}$ the temperature of the magma was below the inversion temperature curve. Near the MgO:FeO ratio of 7:3, and for more FeO-rich pyroxenes, the temperature of the magma was on or above this curve so that a clinopyroxene, pigeonite, abruptly took the place of hypersthene. If the pigeonite were then cooled slowly, upon crossing the inversion temperature curve it would invert to hypersthene, exsolving the excess Wo as oriented augite plates (see Fig. 3).

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* Inversion temperatures measured at one atmosphere pressure. At pressures obtaining under plutonic conditions some modification of the inversion temperatures might occur.

It appears that those pigeonites in hypabyssal rocks which crystallized at a temperature very slightly above the inversion temperature have a much greater tendency to invert to hypersthene with oriented inclusions of augite, than do those more iron-rich pigeonites which probably crystallized farther above the inversion temperature. The Palisades diabase and Win Sill both are examples of this relationship. The probable reason for this is that the earlier pigeonites were held for a relatively long period at, or slightly below, the inversion temperature, thus under conditions ideal for inversion to occur. The later, more iron-rich pigeonites, passed through the inversion temperature relatively rapidly for two reasons. (1) The magma itself was decreasing in temperature rapidly during the closing stages of crystallization (note curve in Fig. 9 for change of temperature of magma with crystallization); and (2) the amount of crystallization is much less, or the magma may be completely solidified so that the heat of crystallization is diminished or zero and is no longer acting as a balance against heat lost by conduction outward from the contacts.

C. *Pyroxenes as Geologic Thermometers.*

From the relationship mentioned in the previous paragraph there becomes available a precise and valuable geologic thermometer. The observed pyroxenes in the Stillwater Complex, for example, must have started crystallization below 1145°C. since normal orthorhombic pyroxene is found in the early differentiates. After approximately 60 per cent of the volume of the magma had crystallized, the magma temperature crossed the inversion curve at the MgO:FeO molecular ratio of 73:27. At this point the temperature was slightly above 1100°C. The total drop in temperature from the start of crystallization to 60 per cent by volume solid appears to have been not more than 40°C. Since the other igneous bodies for which the MgO:FeO ratio at which the magma temperature crossed the inversion curve also lie close to 7:3, the temperature of the magmas of all of them must have been almost identical with that of the Stillwater magma. The inversion curve is relatively flat—a large change in MgO:FeO ratio produces a small change in inversion temperature—so it appears that all of the magmas mentioned above probably were within 10°C. of each other at the start of crystallization. Inasmuch as enstatite or bronzite with oriented plates has never been described, it seems likely that no basaltic magma before extrusion ever reached a temperature above approximately 1140°C. With considerably less certainty it can be said that normal basaltic magmas probably are intruded in all cases at a temperature above 1100°C. It may be noted here that the temperature obtained by this method for the Palisade Sill diabase magma at the time of its intrusion, 1120°C ± 10°C., lies within the limits set by Sosman and Merwin (1913), arrived at in an entirely different manner.

Wager and Deer describe a hedenbergitic clinopyroxene in the Skaergaard intrusion which formed after 98½ per cent of the magma had crystallized. This pyroxene was interpreted on good grounds as an inverted β-wollastonite solid solution. An approximate temperature can also be placed on this inversion, 955°C. as interpolated from data given in $CaO-FeO-SiO_2$ by Bowen, Schairer and Posnjak. Thus a guess can be made for the final temperature of consolidation of a basaltic magma with extreme differentiation. This would place a maximum temperature difference between the start of crystallization and its virtual completion (98½%) at 185°C. The estimated change in temperature of the magma with crystallization, as shown in Fig. 9, was based on this value.

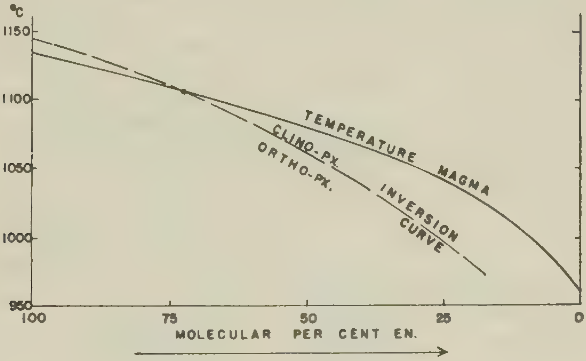

FIG. 9

A rough estimate of temperature may also be based on the calcium-rich clinopyroxenes. These clinopyroxenes occurring in contact metamorphic deposits, such as skarn, and in veins, lie very close to $Wo_{50}(En, Fs)_{50}$ in composition. They are known to have crystallized at relatively low temperatures compared to basaltic magmas. The calcium-rich clinopyroxene phases of basaltic magmas (excluding phenocrysts of effusives) have compositions for the magnesian varieties of $Wo_{40}(En, Fs)_{60}$ and for the more iron-rich varieties of $Wo_{30}(En, Fs)_{70}$. The clinopyroxenes of lamprophyres seem to lie near $Wo_{50}(En, Fs)_{50}$ indicating a very low temperature for such magmas. The clinopyroxene found rarely in rocks of the ultramafic magma suite (Hess 1939) is also near $Wo_{50}(En, Fs)_{50}$ so far as the writer has been able to determine, this checking his previous conclusion (provided these clinopyroxenes are primary) that such magmas have relatively low temperatures.

D. Course of Crystallization of Pyroxenes from Mafic Magmas.

It has been previously shown that there is relatively little difference between pyroxene trends in mafic magmas crystallizing at depth, near the surface, or at the surface. Except for the phenocrysts in effusives there is no difference chemically. It is, therefore, possible to use the data derived from a large number of new analyses of Stillwater clinopyroxenes, plus the published analyses of Wager and Deer for the Skaergaard intrusion, to give the chemical changes which take place with progressive fractional crystallization. By chance the Stillwater and Skaergaard complement each other nicely. The upper portion of the Stillwater is covered and the lower portion of the Skaergaard is hidden, but the pyroxenes at the top of the former and base of the latter are closely similar so that the two sets may be joined to give the complete trends (see Table 2).

TABLE 2

Roof		Clinopyroxene	Orthopyroxene	Remarks
Skaergaard	2500 meters	$Wo_{30}\ En_2\ Fs_{68}$	absent	Limit two pyroxene field—↴
	1800 meters	$Wo_{27}\ En_{23}\ Fs_{50}$	absent	
	1200 meters	$Wo_{32}\ En_{32}\ Fs_{36}$	$Wo_9\ En_{39}\ Fs_{52}$[2]	
	500 meters	$Wo_{42}\ En_{40}\ Fs_{18}$[1]	$Wo_9\ En_{50}\ Fs_{41}$[2]	Inverted
	0 meters	not given	$Wo_9\ En_{54}\ Fs_{37}$[2]	
Covered				Pigeonites
Stillwater[3]	5400 meters	$Wo_{41}\ En_{45}\ Fs_{14}$	$Wo_9\ En_{64}\ Fs_{27}$	
	4750 meters	$Wo_{41}\ En_{47}\ Fs_{12}$	$Wo_4\ En_{73}\ Fs_{23}$	
	2550 meters	$Wo_{41}\ En_{49}\ Fs_{10}$	$Wo_4\ En_{75\frac{1}{2}}\ Fs_{20\frac{1}{2}}$	
	400 meters	$Wo_{37}\ En_{56}\ Fs_7$	$Wo_4\ En_{82}\ Fs_{14}$	
Floor				

[1] As recalculated by the present writer allowing for Wo content in hypersthene impurity.

[2] Based on petrographical description and optical properties as given.

[3] Stillwater specimens represent either chemical analyses or pyroxenes between two analyzed specimens, estimated by optical properties.

In Fig. 10 are shown the compositions of the chemically analyzed pyroxenes of the Stillwater Complex, Bushveld Complex, and the Skaergaard intrusion, plus a number of analyses of typical pyroxenes from other igneous bodies as taken from the literature. The trend of crystallization of pyroxenes is clear and has already been discussed in the descriptive

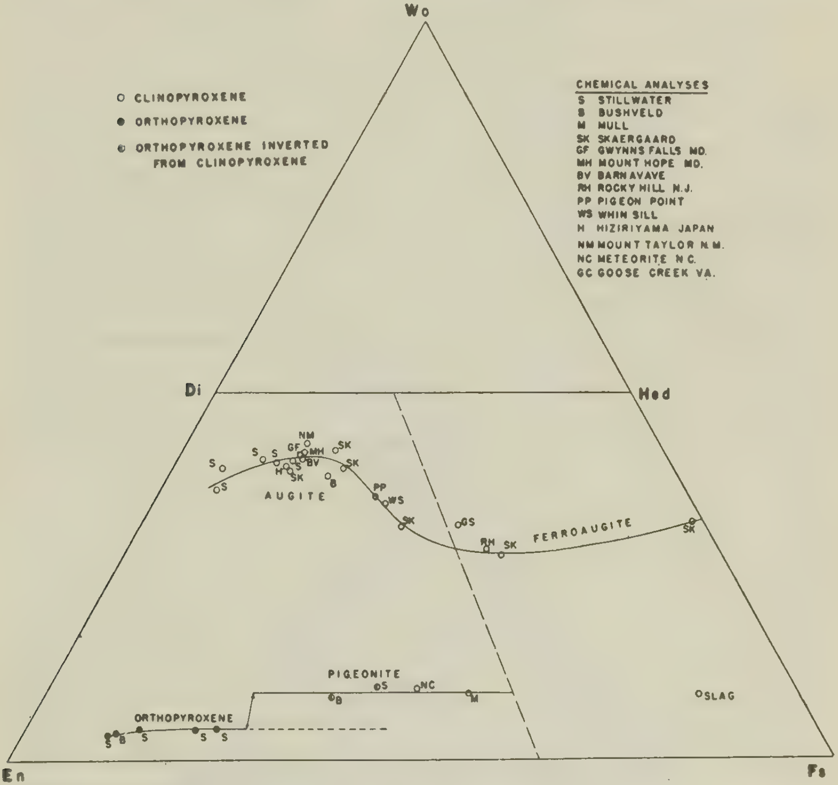

FIG. 10

portion of this paper. In Fig. 11 the relation between the composition of the augitic clinopyroxene and the orthopyroxene or pigeonite in equilibrium with it, in a given rock specimen is shown.

If a line joining the two pyroxenes of a given specimen be extended upwards to the En-Wo composition line it will intersect that line at approximately $En_{25}Wo_{75}$. Why this relationship holds the writer does not know. It is, however, a rather convenient fact to know since it may be used to predict the composition of one pyroxene from an igneous rock if the other pyroxene be known from chemical analysis or by determination from

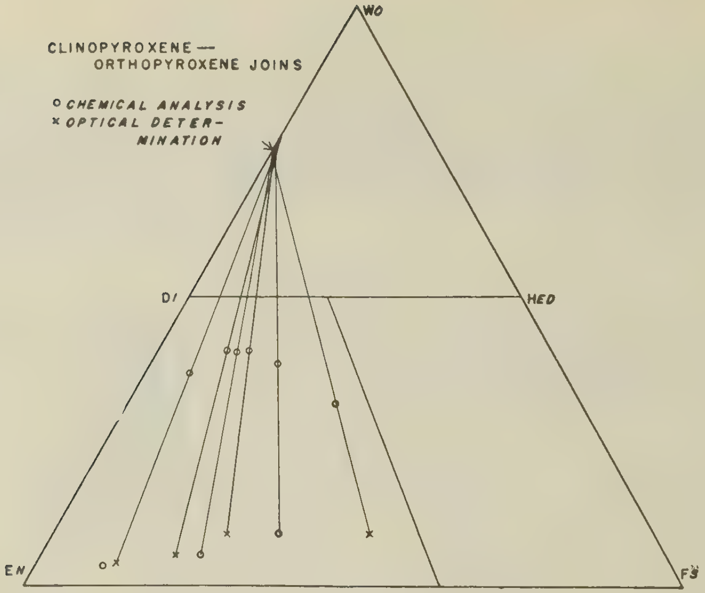
WO
CLINOPYROXENE — ORTHOPYROXENE JOINS
○ CHEMICAL ANALYSIS
× OPTICAL DETERMINATION
DI
HED
EN
FS

Fig. 11

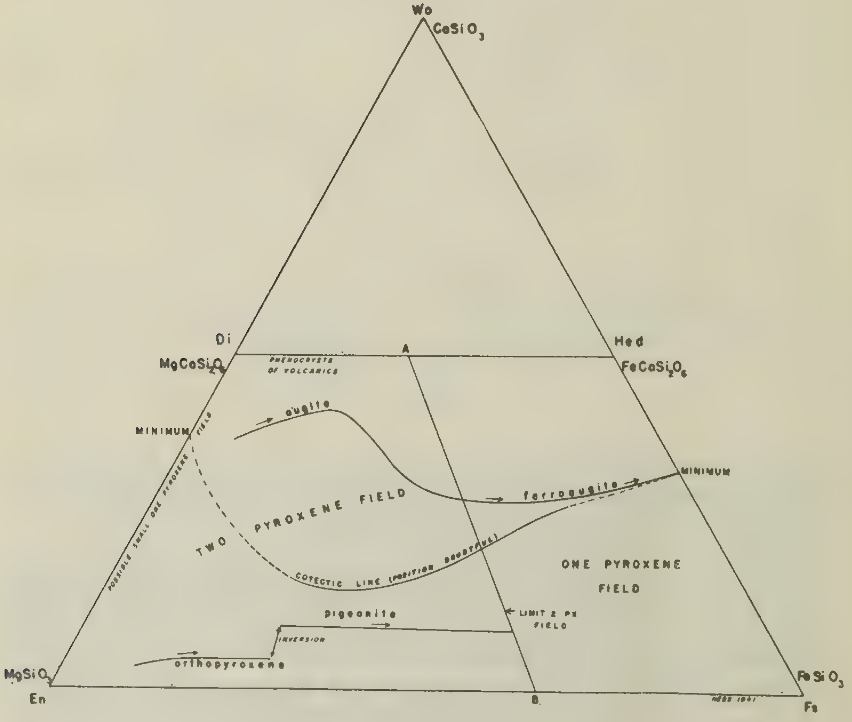
Wo
$CaSiO_3$
Di
$MgCaSi_2O_6$
Hed
$FeCaSi_2O_6$
A
PHENOCRYSTS OF VOLCANICS
MINIMUM
POSSIBLE SMALL ONE PYROXENE FIELD
augite
MINIMUM
ferroaugite
TWO PYROXENE FIELD
COTECTIC LINE (POSITION DOUBTFUL)
ONE PYROXENE FIELD
pigeonite
LIMIT 2 PX FIELD
INVERSION
orthopyroxene
$MgSiO_3$
En
B
HESS 1941
$FeSiO_3$
Fs

Fig. 12

optical properties. It may also be used to estimate the composition of the pyroxenes in a rock for which the normative Wo:En:Fs ratio is known.

In Fig. 12 the pyroxene trends, the limit of the two pyroxene field and the two pyroxene boundary curve of Tsuboi (or cotectic) are all shown. The pyroxene portions of both the system En-Di and Fs-Hed are of the type representing a solid solution series with a minimum, according to the laboratory data of Bowen and Schairer. The two pyroxene boundary has been extended by a dashed line to join the minimum on each of the two above mentioned systems. Whether the cotectic line should be joined to the minima in this manner is not known, but it appears to be a likely approximate relationship. The position of the two pyroxene line itself is only an approximation since it is based on uncertain data. In order to locate it one must know the Wo:En:Fs ratio of a number of magmas and one must also know whether a lime-rich clinopyroxene or a lime-poor orthopyroxene or pigeonite crystallized first from that magma. Uncertainty regarding the position of this curve is related to the highly complex relations in natural magmas. The normative Wo:En:Fs ratio of fresh, fine grained, or glassy, nonporphyritic rocks might be used to locate the curve. The fact that TiO_2 and Fe_2O_3 are present in the pyroxenes themselves, however, and not all in magnetite and ilmenite, is a source of error in the location of the curve. It seems to be more satisfactory to calculate the Wo:En:Fs ratio without deducting FeO for ilmenite and magnetite where the TiO_2 and Fe_2O_3 are small in amount, and deducting only part of the FeO where they are present in greater amounts. Similarly, Al_2O_3 in the pyroxene appears as anorthite in the norm and also is a source of error. Furthermore, the presence of calcium in the magma which eventually goes into anorthite and the presence of magnesium and iron which eventually go into olivine might well have some effect on the composition of the pyroxene crystallizing even though they, later on, combined in minerals other than pyroxenes. In spite of all these difficulties it is possible to construct an approximate curve.

Following the reasoning of Tsuboi, after early crystallization of one pyroxene the second should appear and fractional crystallization should produce a successive series of liquids which would lie along the curve. If the Wo:En:Fs ratios for the more iron-rich plateau basalts be plotted, they do show a concentration along the line as given in Fig. 12.

Following the two pyroxene boundary curve to its extremity on the Ca-Fe side of the diagram, it has been joined to the minimum of Bowen's, Schairer's and Posnjak's hedenbergite-ferrosilite diagram. There is good justification for this since the final clinopyroxene of the Skaergaard intrusion has almost exactly the composition of the minimum point. The extension of the curve to the similar minimum of the diopside-enstatite diagram was placed on the figure by analogy and has no significance so far as basaltic magmas are concerned, since these never have an MgO:FeO ratio greater than 7:3.

It has very generally been supposed that a complete series of solid solutions exists (at least at the high temperatures of laboratory investigation of dry melts) between the four components of the pyroxene series, En-Fs-Di-Hed. Justification for this view is found in the fact that the three investigated pairs, En-Di, En-Fs, and Fs-Hed bounding three sides of the field all show such a relationship. The central portion of the field has not been investigated in the laboratory, but it has been thought that natural occurrences, namely the groundmass pyroxenes of basalts and andesites, supported such an assumption. Strong evidence has been given in this paper to show that this assumption is incorrect for the natural magmas and that two pyroxene phases are normally present, at least between MgO:FeO ratios of approximately 75:25 and 35:65 (see Fig. 10). It seems likely the two pyroxene field will extend at least to a line very close to En-Di before changing over to a single series of solid solutions with a minimum if such a change takes place at all at magmatic temperatures. The trend of igneous clinopyroxenes upon approaching En-Di suggests that such a change might take place in natural magmas if magmas sufficiently iron-poor and calcium-rich could be found. Relations, however, are complicated by the presence of orthorhombic rather than monoclinic $MgSiO_3$ in rocks. On the iron-rich side of the two pyroxene field, the change represented in natural occurrences in rocks (namely the abrupt disappearance of the lime-poor pyroxene phase, pigeonite and the continued crystallization of the augitic phase along a trend which terminates almost exactly at Bowen's and Schairer's minimum in the Fs-Hed join) clearly indicates the chemical change from a field with two pyroxene phases to a field of solid solutions with a minimum. This will be further considered in a series of diagrams.

Perhaps the simplest means by which the proposed relations within the En-Fs-Di-Hed field can be discussed is by construction of a series of hypothetical equilibrium diagrams joining the En-Fs series with the Di-Hed series. The most fundamental section is one between $En_{50}Fs_{50}$ and $Wo_{50}En_{25}Fs_{25}$. This is given in Fig. 13. It must be clearly understood that this is not a true binary but a purely schematic type of diagram since the third dimension is not shown. Actually all liquidus points are far more iron-rich than solidus points, but here they are for convenience all shown in one plane. Nevertheless, the diagram illustrates qualitatively the relations in the portion of the field under consideration.

If the composition lies to the left of *M*, pigeonite will crystallize first, and continue to do so until point *M* is reached where it has the composition *L* and where it will be joined in crystallization by augite of composition *N*. After all of the liquid is used up there will remain a mixture of two solid phases, pigeonite and augite. With further decrease in temperature pigeonite becomes unstable and will invert to hypersthene *T*, if cooling is slow enough to permit this to occur. The change in composition from *S* to *T* in an inversion interval will result in the exsolution from *S* of an augite of composition *R*. This exsolved augite, as has been described previously, forms oriented plates in the hypersthene.

If the original composition lies to the right of *M*, augite will crystallize first and after the composition of the liquid reaches *M*, pigeonite will start to crystallize. From this point on the sequence of events is the same as described in the previous paragraph. With continued slow cooling hypersthene changes in composition toward *X*, exsolving a Di-Hed pyroxene approaching *Y* in composition as fine lamellae parallel to (100), and augite similarly changes in composition toward *Y*, exsolving hypersthene which in turn forms fine lamallæ in the augite parallel to (100) or (001). As a rule this late exsolution does not go to completion, at least in the augite, because pure Di-Hed pyroxenes (+lamellæ) do not result, but rather a phase midway between *N* and *Y*. Apparently exsolution is too slow or conversely the rock cools too quickly to permit the process to go to completion, and the dissolved material will be held in solution (metastably?) indefinitely once the rock has become cold.

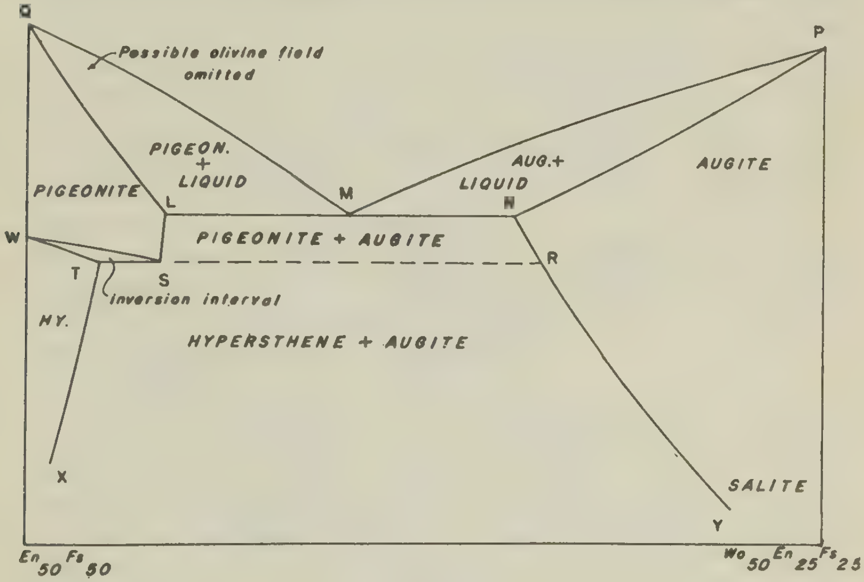

Fig. 13

We may now consider how the above relations are modified in more magnesian and in more iron-rich crosssections between En-Fs and Di-Hed. If we proceed from $En_{50}Fs_{50}$-$Wo_{50}En_{25}Fs_{25}$ toward En_{100}-$Wo_{50}En_{50}$ the main change in the diagram for natural occurrences would be as follows: The inversion curve *WST* would move upwards relative to *QM* and would finally cross *QM* at a MgO:FeO molecular ratio near 7:3. This relationship between the inversion temperature and magma temperature is more clearly shown in Fig. 9. After *WST* crosses *QM*, hypersthene will crystallize with augite and no pigeonite will be formed since crystallization is proceeding at a temperature below the stability field for pigeonite *at the MgO:FeO ratio obtaining.*

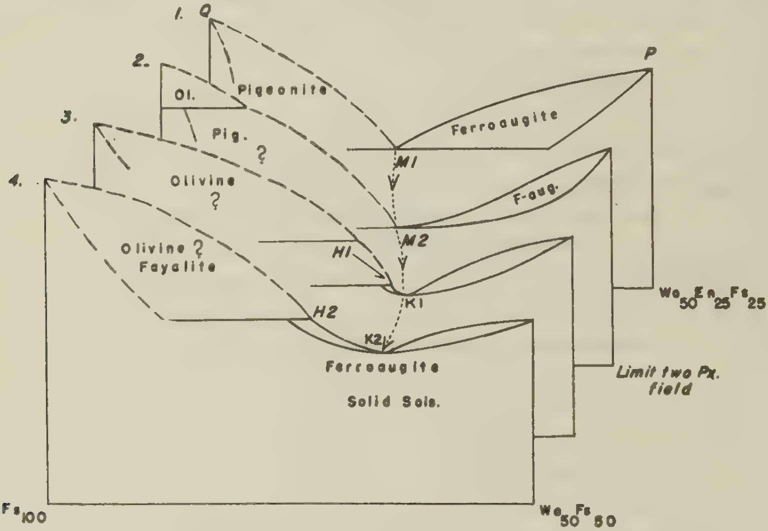

FIG. 14

Proceeding in the other direction from $En_{50}Fs_{50}$-$Wo_{50}En_{25}$ Fs_{25} toward the more iron-rich portion of the field the following changes are thought to occur. Upon crossing the limit of the two-pyroxene field, *AB* Fig. 13, the augite or ferroaugite side of the diagram changes. The nature of the change is shown in Fig. 14.

Crosssection No. (1) in this figure is the same as the previous figure, and No. 4 is in part Bowen's and Schairer's diagram for Fs-Hed. Section No. 2 presents the relations at the boundary of the two-pyroxene field and No. 3 the relations just beyond the two-pyroxene field.

From section No. 1 in Fig. 14 to No. 2 the main change postulated is a narrowing of the area between the solidus and liquidus of ferroaugite. The significant change occurs between No. 2 and No. 3 where the ferroaugite liquidus and solidus bend slightly downwards at the left hand side of the ferroaugite field developing into a solid solution series with a minimum. Crystallization in No. 1 and No. 2 had been proceeding along the cotectic line M_1–M_2 with the separation of pigeonite and ferroaugite together. At the boundary of the two-pyroxene field a change takes place the nature of which can be seen in No. 3. As a result of this change pigeonite at H in the diagram reacts with the liquid to form a ferroaugite solid solution.* After all of the pigeonite is used up, ferroaugite will continue to crystallize directly from the magma and its composition will gradually move to the minimum line K_1–K_2. It will continue to change in composition along the line K_1–K_2 as fractional crystallization proceeds until K_2 is reached, or the entire liquid becomes solid. Wager's and Deer's final clinopyroxene is practically at the point K_2. It may also be noted that an olivine field presumably appears on the left hand side of the diagram which increases in size until at the Fs-Hed join the pigeonite field has been completely removed.

It is possible as previously mentioned that a similar type of change occurs at the other side of the two-pyroxene field where the change takes place with increasing temperature to a one-pyroxene, diopside-clinoenstatite solid solution series with a minimum.

E. Summary of Main Features in Pyroxene Relations of Mafic Magmas

1. The pyroxenes of plutonic, hypabyssal and effusive mafic igneous rocks are chemically the same except for the phenocrysts of certain effusives which have been changed from augite towards diopside.
2. In a considerable portion of the field En-Fs-Di-Hed the En-Fs clinopyroxenes show limited solid solution in the Di-Hed and *vice-versa* so that both pigeonite and augite may crystallize together and commonly do.
3. Orthopyroxene bears a mutually interchangeable relationship to pigeonite. The more magnesian crystals are orthorhombic since the inversion temperature (clino- to ortho-) is above magmatic temperatures. The more ferriferous crystallize as pigeonite since the inversion temperature is below magmatic temperatures for such compositions.
4. With slow cooling pigeonite inverts to hypersthene containing oriented plates of clinopyroxene exsolved from it.
5. The most ferriferous clinopyroxenes (beyond the two pyroxene field) probably form a continuous solid solution series with a minimum, thus ferroaugite is never accompanied by pigeonite under equilibrium conditions.

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* Early pigeonite phenocrysts resorbed (corroded outlines), Mull and Hakone.

6. The trend of crystallization of both the pyroxene phases is essentially from magnesian to iron-rich.

ACKNOWLEDGMENTS

New chemical analyses, and thin sections which were made use of in this investigation as well as field work by the writer were all financed by funds granted for that purpose by Princeton University.

The writer wishes to express his indebtedness to his colleague, A. F. Buddington, for much helpful discussion during the course of the work and for a criticism of the manuscript before publication.

The writer is grateful to A. N. Winchell and E. S. Larsen for reading the manuscript and suggesting a number of changes and corrections which have been a great assistance in completing and improving the paper. He also wishes to thank H. Berman, C. S. Hurlbut and Harold James for criticism of specific parts of the manuscript.

W. F. Foshag and E. P. Henderson of the U. S. National Museum, F. F. Grout, A. N. Winchell, J. T. Stark and A. L. Howland all lent specimens to the writer in connection with this investigation for which assistance he is duly grateful.

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COMPOSITION AND PROPERTIES OF SOME NEW ZEALAND GLAUCONITES

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Abstract

Seven new analyses of pure glauconites separated from sediments of Upper Cretaceous and Tertiary age, have been analyzed and their optical data determined. From this it has been possible to construct curves showing the variation of α, γ and $\gamma-\alpha$, with increasing content of Fe_2O_3. Finally it is shown that the analyses fit the structural formula derived for glauconite by Gruner.

During an investigation of the distribution and quantity of greensands of the Upper Cretaceous and Tertiary formations in New Zealand, a considerable number of samples was collected with a view to a mineralogical study of glauconite. Of the specimens collected, seven have been used in the present study.

The samples were crushed and passed through a 60-mesh sieve, and then concentrated to some extent by shaking on a 100-mesh; material having a grain-size greater than 60-mesh or less than 100-mesh was rejected as too impure. The glauconite in the sand of this grade was then further concentrated by electro-magnetic treatment and subsequently purified by flotation in bromoform or bromoform-benzene mixtures. Clerici solution was not used in preparing any samples of glauconite for analysis, for Gruner (1935, p. 704) has found experimentally that in the case of a sample of glauconite boiled in thallium nitrate solution for four hours, about 25% of the K ions were replaced by thallium ions, with resultant increase in the specific gravity from 2.81 to 3.02. The behavior of glauconite in Clerici solution is similar to that of the stilpnomelane minerals, for Holzner (1933) found that thallium was absorbed into the structure to such an extent that analysis showed 9.83% Tl_2O, while K_2O was reduced from 2.20 to 0.29%. Centrifuging was necessary in two cases, while one specimen of glauconitic greensand, rich in coarse biotite, was separated from the latter constituent by the simple procedure of vibration on cardboard, the mica remaining on the board and the glauconite rolling off. Microscopic inspection was carried out before chemical analysis was undertaken.

The glauconite content of the samples ranges between wide limits, from about 10% in *P.* 4640,* a glauconitic limestone from Milburn

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* Numbers *P.* 4640 etc. refer to specimens in the mineral and rock collections of the New Zealand Geological Survey, Wellington.

Quarry, Otago, to about 90% in *P.* 4895, a greensand from Makerewau Creek, Mangatu Survey District. The other samples used in this study were glauconitic sandstones and siltstones, containing approximately 40–60% of glauconite. This group is typical of many of the greensand deposits of New Zealand, which in places reach a thickness possibly in excess of 200 feet.

The glauconite grains were rounded, spongy, concertina-shaped, or moulded into coprolites in the manner described by Galliher (1935*a* and *b*). The individual grains are made up of microcrystalline aggregates of platelets of glauconite, occasionally with a regular radiate arrangement, though more frequently with some suggestion of optical continuity as

TABLE I. ANALYSES OF PURE GLAUCONITES

	1.	2.	3.	4.	5.	6.	7.
SiO_2	49.07	52.64	49.29	43.33	48.54	47.42	47.15
Al_2O_3	10.95	5.78	3.17	7.27	7.82	7.19	6.20
Fe_2O_3	15.86	17.88	21.72	24.87	17.50	22.64	21.50
FeO	1.36	3.85	3.19	2.90	3.07	3.39	3.76
TiO_2	0.15	0.16	0.12	0.20	0.10	0.10	0.14
CaO	0.07	0.12	0.74	0.10	0.68	0.27	0.46
MgO	4.49	3.43	3.85	2.95	3.26	2.28	2.80
Na_2O	0.13	0.18	0.12	0.02	0.22	0.05	0.13
K_2O	7.51	7.42	6.02	6.00	5.87	7.46	6.98
MnO	tr.(?)	tr.	tr.	tr.	tr.	tr.(?)	tr.(?)
P_2O_5	0.19	0.18	0.32	0.15	0.14	0.22	0.19
Cr_2O_3	0.07	n.d.	n.d.	n.d.	0.03	0.04	0.05
S	0.06	n.d.	n.d.	n.d.	0.05	0.05	0.06
BaO	nt.fd.	n.d.	n.d.	n.d.	nt.fd.	nt.fd.	0.04
ZrO_2	nt.fd.	n.d.	n.d.	n.d.	nt.fd.	nt.fd.	nt.fd.
H_2O+	6.63	5.86	7.21	6.22	6.00	6.07	6.47
H_2O-	3.66	2.83	4.60	5.94	6.71	3.01	4.20
	100.20	100.33	100.35	99.95	99.99	100.19	100.13
Sp. Gr.	2.687	2.708	2.580	2.735	2.555	2.790	2.770

1. Lower band, Milburn Lime and Cement Co.'s Quarry, Milburn, Table Hill Survey District, Otago Land District. *P.* 4640.
2. From thin band, Makerewau Creek, Mangatu Survey District, Gisborne Land District. *P.* 4895.
3. Whare Flat, East Taieri Survey District, Otago Land District. *P.* 6034.
4. Abandoned railway cutting, Elephant Hill Survey District, Canterbury Land District. *P.* 5392.
5. Kakaho Creek, Otepopo Survey District, Otago Land District. *P.* 6035.
6. North end of Otepopo railway tunnel, Otepopo Survey District, Otago Land District. *P.* 5621.
7. Northern bridge, Waianakarua, Otepopo Survey District, Otago Land District. *P.* 5618. A trace of CO_2 was present.

shown by inspection after insertion of a gypsum plate. The diameter of the platelets averages approximately 0.01 mm. though in *P.* 6035, platelets up to 0.05 mm., with an average of 0.02 mm. were observed. Single crystals, however, are exceedingly rare and long and careful searching was necessary to find these, except in the case of *P.* 6035; a preparation of this specimen showed a number of crystal fragments.

It was not found possible to determine the hardness with any accuracy but grinding tests certainly showed considerable differences. The specific gravities of the analyzed specimens ranged from 2.55–2.79.

The complete chemical analyses of seven specimens of glauconite are given in Table I. Inspection of the analyses in this table reveals a noteworthy range in the percentage of SiO_2, and the figure 52.64% in No. 2 (*P.* 4895) would suggest that a little quartz might have been present as an impurity, though microscopic examination did not reveal this. There is considerable alumina in No. 1, but this is not sufficiently high to warrant comparison with the aluminous glauconite, skolite (Table II, analysis 11), described by Smulikowski (1936). The iron in all examples is mainly in the ferric condition, with ferrous iron not exceeding 3.85%. TiO_2 is persistently low but fairly constant in amount. It should be noted that Allen (1937, p. 1181) observed rutile needles in two glauconites from Monterey Bay, California, thus accounting for 0.59% and 0.30% of TiO_2 found in the analyses. Microscopic examination of the New Zealand glauconites, however, failed to reveal any trace of rutile as a possible source of the titanium.

Lime is consistently low and does not in any example exceed 0.74% but is usually much less than this figure. After allotting sufficient CaO for the P_2O_5 determined in each analysis, slight excess of CaO remains in three cases only, viz. No. 3 (0.35%), No. 5 (0.45%) and No. 7 (0.2%). The mode of occurrence of the tri-calcium phosphate is not at all clear. An experiment was carried out as follows, in order to determine if grains of apatite were associated with the glauconite: the granular glauconite was treated with dilute HNO_3 (2%) and warmed for ten minutes on the water-bath. The liquid was then decanted and the glauconite well washed, crushed and again treated with HNO_3. The glauconite was filtered off and on test the second filtrate gave a strong phosphate reaction. At present it can only be suggested that the phosphatic solutions percolating through the sediments have, to some extent, intimately penetrated the crystalline glauconite aggregates or granules and deposited films of $Ca_3(PO_4)_2$ over the surfaces of the minute platelets. All good analyses of carefully prepared glauconite show a low content of CaO and apparently as Gruner (1935, p. 713) points out, the crystal structure would allow only a fraction of one per cent of calcium to be present.

TABLE II

	8.	9.	10.	11.	12.	13.	14.
SiO_2	48.66	49.05	55.95	49.09	48.12	50.58	49.47
Al_2O_3	8.46	7.96	11.56	18.17	9.60	6.72	5.59
Fe_2O_3	18.80	19.66	9.99	6.42	19.10	19.50	19.46
FeO	3.98	0.75	2.02	2.56	3.47	2.96	3.36
TiO_2	nt.dt.*	nt.dt.	nt.dt.*	0.21	nt.dt.	nt.dt.	nt.dt.
CaO	0.62	2.34	3.95	1.03	0.76	0.34	0.60
MgO	3.56	1.17	6.77	3.10	2.36	4.10	3.96
Na_2O	nil	0.78	0.61	0.23	0.22	0.04	0.16
K_2O	8.31	6.18	4.12	5.62	7.08	8.26	8.04
MnO	0.01	nt.dt.	nt. dt.	tr.	nt.dt.	nt.dt.	nt.dt.
P_2O_5	0.12	nt.dt.	0.18	tr.	nt.dt.	0.27	1.06
CO_2	nt.dt.	nt.dt.	nt.dt.	nt.dt.	nt.dt.	0.30	0.56
H_2O+	4.62	11.79	3.22	13.47	10.06	7.76	8.54
H_2O-	1.94		1.60				
	99.08	99.68	99.97	99.90	100.77	100.83	100.80

8. St. Joseph Lead Co. Mines, St. Joseph, Mo., U.S.A. G. V. Brown, *analyst* (Ross, 1926, p. 10, Table II, No. 11).
   * $TiO_2=0.10$ determined by R. T. Rolufs (see V. T. Allen, 1937, p. 1181).
9. Huntington, Oregon, E. P. Henderson, *analyst* (Ross, 1926, p. 10, Table II, No. 13). Note that the figures for Al_2O_3, Fe_2O_3, Na_2O and K_2O were probably transposed; they have been corrected by Gruner, 1935, p. 706, Table 3.
10. Firm type, Monterey Bay, California, A. A. Hanks, *analyst* (Galliher, 1935*b*, p. 1359).
    * $TiO_2=0.59\%$ determined by R. T. Rolufs (see V. T. Allen, 1937, p. 1181).
11. Skolite, a new mineral of the glauconite group (K. Smulikowski, 1936).
12. Lewes, Sussex, E. G. Radley, *analyst* (see A. F. Hallimond, 1922, p. 331).
13. Sewell, N. J., Hornerstown marl, glauconite grains separated magnetically from the residues of washed greensand, R. K. Bailey, *analyst* (see G. R. Mansfield, 1922, p 128).
14. Elmwood Road, N. J.; as in No. 13 above.

The figure for magnesia is very constant and comparison with other analyses substantiates the evidence that it never becomes an important constituent. In all the New Zealand specimens, Na_2O is quite unimportant and the analyses do not provide any further evidence of the existence of a soda-bearing glauconite, which Hallimond (1922, pp. 332–333) suggests may occur. Ross (1926, p. 10, Table II) quotes four analyses of glauconite containing over 1% Na_2O, No. 13 in his table being shown as containing 6.18% Na_2O; it seems reasonable to suppose, however, that in this latter case, the Na_2O and K_2O figures have been transposed (this paper, Table II, analysis 9).

The determination of small amounts of Cr_2O_3 in four of the New Zealand glauconites is of interest, but owing to the failure of most analysts to estimate the quantity of this constituent, no further comment can be made now.

The amount of water evolved at temperatures greater than 105°C. is remarkably constant but there is considerable variation in that given off at temperatures below that figure. Ross (1926, p. 8) has carefully investigated the water content of an analyzed glauconite from Bonneterre, Mo., U.S.A., at different temperatures, and the dehydration curve thus determined clearly shows a break at 280°C., 3.30% H_2O having been given off below that temperature and 3.26% H_2O above it.

The writers have carried out a series of experiments in order to discover the solubility of glauconite in acids of different concentrations. Granular glauconite, that is uncrushed material, when treated with 1% HCl solution on the water-bath for 15 minutes, was considerably attacked and further, such action appeared to be selective. Quantitative data were obtained by treating a sample of slightly impure glauconite obtained by electro-magnetic separation from the Waianakarua greensands, with different strengths of hydrochloric acid; the solutions so obtained were then analyzed for the main constituents (see Table III).

TABLE III

	3%	6%	12%	24%
SiO_2	5.64	7.60	8.06	6.00
Al_2O_3	1.58*	2.42*	3.82*	5.12*
Fe_2O_3 FeO	7.48	14.28	21.34	27.64
TiO_2	0.03	0.10	0.14	0.20
CaO	0.68	0.68	0.70	0.70
MgO	0.96	1.24	1.78	2.42
Na_2O K_2O	1.20	2.02	3.60	5.36
	17.57	28.34	39.44	47.44
Insol. res.	70.90	60.32	49.32	40.94

* Includes any soluble P_2O_5 and Cr_2O_3.

A sufficient quantity of pure Waianakarua glauconite (Table I, No. 7) was available in order to determine its solubility with one concentration of HCl (24%), and the amounts of the main oxides dissolved are given in Table IV.

In all the above tests the finely powdered samples were heated with acid solutions for two hours at 100°C. No attempt was made to dissolve out with alkali from the residue any silica which had gelatinized during the acid treatment. However, it is evident from inspection of Tables III and IV that, especially in the case of the stronger acids, most of the insoluble residues must consist of gelatinous silica.

At this stage it might be pertinent to examine critically a method used by Schneider (1927, pp. 301–302) for the preparation of a sample of pure glauconite. In order to effect a separation of glauconite from a mixture of that mineral and quartz, he suggests digestion with HCl and then NaOH. The colloidal suspension of "glauconite"* is then made slightly acid, coagulation results and the precipitate of "glauconite" is then washed, dried at 110°, powdered and analyzed. Now the writers' work has shown conclusively that dilute HCl selectively attacks glauconite, dissolving a portion of each oxide present in varying amounts. How Schneider's separation was carried out remains incomprehensible to the present writers. If Schneider uses the term glauconite (1927, first line on p. 302) loosely for a solution of glauconite in HCl, it is still not clear how he was able to estimate K_2O, if this precipitate was washed as he states. Again it is not clear how H_2O could be determined in this preparation, for a temperature of 110° could not dehydrate the gelatinous silica and the R_2O_3 precipitate. The base exchange or zeolitic properties of glauconite are well known and in view of this, it is most surprising that Schneider's "glauconite" prepared in this way, should not have had a considerable amount of the potash replaced by soda.

TABLE IV. OXIDES DISSOLVED FROM PURE GLAUCONITE

	24% HCl
SiO_2	7.30
Al_2O_3	5.66
Fe_2O_3 FeO	24.80
TiO_2	0.13
CaO	0.46
MgO	2.66
Na_2O	0.08
K_2O	6.68
	47.77
Insol. res.	42.06

Shaking tests carried out for periods up to 8 hours bear out the work of Mansfield (1922, pp. 116–118) on the cause of the cloudiness developed in the liquid when grains of glauconite are agitated or stirred in pure water. Pure samples of glauconite granules were shaken with water in a rotary shaker, revolving at 35 revolutions per minute. A period of five minutes was sufficient to produce considerable cloudiness and after a period of one hour, a very dense cloudiness was produced. Shaking was continued for a further two hours and then the fine suspension was decanted and the liquid evaporated to dryness on a water-bath. Microscopic inspection proved that this cloudiness was entirely caused by a suspension of finely comminuted glauconite. The glauconite granules were recovered from this first shaking, washed and shaken with water for another period of three hours, with similar results. It appears to the writers that this process could be continued until the granules were reduced to a grain-size where the cushioning effect of the water would prevent mutual attrition.

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* The quotation marks are the present authors'.

OPTICAL PROPERTIES OF GLAUCONITE

Because the glauconite granules are composed of aggregates of very minute platelets determination of the optical properties was not easily accomplished. All the optical data that could be obtained for the seven analyzed glauconites are given in Table V.

The α and γ refractive indices were determined in sodium light but owing to the nature of the material dealt with, it is stressed that the accuracy will be of the order of ± 0.005. Further, in view of the small optic axial angle and the fineness of the material it was impossible to measure β as distinct from γ. The figures given for the optic axial angle, 2V, likewise are not more accurate than $\pm 5°$. In all examples a fair cleavage parallel to the γ-vibration direction was observed; extinction appeared to be straight with reference to this direction.

TABLE V. OPTICAL PROPERTIES OF GLAUCONITES.

	1.	2.	3.	4.	5.	6.	7.
$\alpha=$	1.601	1.602	1.592	1.610	1.600	1.602	1.604
$\gamma=$	1.615	1.618	1.614	1.634	1.621	1.627	1.624
$\gamma-\alpha=$	0.014	0.016	0.022	0.024	0.021	0.025	0.020
2V=	10°	10–20°	10°	10°	13°	12°	10–20°
Opt. sign:	neg.	neg.	neg.	neg.	neg.	neg.	neg.
Pleochroism, α:	yellowish-green	bright green	yellowish-brown	yellowish-green	pale yellowish-green	yellowish-green	very pale green
γ:	deeper yellowish-green	bright bluish-green	olive green	bright green	deep green	olive green	olive green
Absorption:	$\gamma>\alpha$	$\gamma>\alpha$	$\gamma>\alpha$	$\gamma>\alpha$	$\gamma>\alpha$	$\gamma>\alpha$	$\gamma>\alpha$
Elongation:	positive	positive	positive	positive	positive	positive	positive

The optical properties correspond closely with the data obtained by Ross (1926, pp. 3–4) and attempts to correlate the Fe_2O_3 content with the refractive index data have been moderately successful (Fig. 1). It will be noticed that the refractive indices of specimen No. 3 are somewhat different from the other values plotted, though the analysis reveals no obvious cause for this discrepancy. Except for No. 3, the γ values all lie in a fair position but this happy state was not attained so completely for the α values. It is suggested that the determination of γ is more readily and accurately carried out than the determination of α, on account of the micaceous nature of the mineral. Hence, the poorer alignment of the α points will probably be due to the difficulty of determining the minimum value for the refractive index ellipsoid. Data taken from the literature have been added to those determined by the writers; these are the points R and R' (Ross, 1926, p. 4). The values for R fit the curves quite well but unfortunately Ross only gave the optical constants for R' to the second place, so that plotting these values on Fig. 1 will be somewhat inaccurate. The birefringence for R' was not plotted. The curves certainly suggest that a series exists, grading from the normal ferruginous glauconites to the aluminous glauconites; the latter are classed by Smulikowski (1936) as pholidoides, and in this group he includes his mineral skolite.

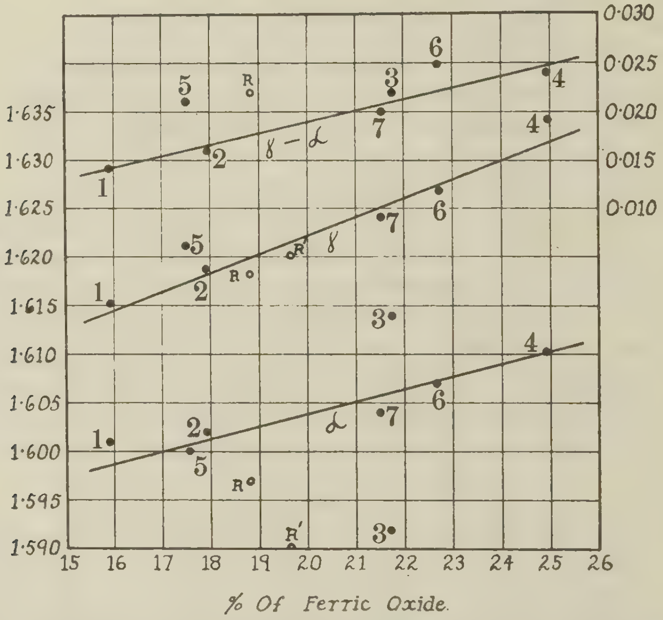

FIG. 1. Relation between refractive indices and content of Fe_2O_3 in glauconite.

It must be pointed out that these curves, based on so few data, can only be provisional in the meantime, but the writers consider that the data obtained so far should be plotted and curves drawn so that as new information is obtained, this may be added and the curves corrected. It is proposed to name the series the glauconite series and the two end-members are to be termed aluminous glauconite (AlGl) and glauconite (Gl).

FORMULA OF GLAUCONITE

The derivation of a formula for glauconite has occasioned considerable discussion. The formulae suggested by some authors are given below:

Clarke (1908):
$Fe'''KSi_2O_6+aq$, in which some iron is replaced by aluminum and other bases partly replace potassium.
Hallimond (1922):
$R_2O \cdot 4(R_2O_3, RO) \cdot 10\,SiO_2 \cdot n\,H_2O$.
Ross (1926):
From $2H_2O \cdot K_2O \cdot 2(Mg, Fe)O \cdot 2(Fe, Al)_2O_3 \cdot 10SiO_2+3H_2O$ to $2H_2O \cdot K_2O \cdot (Mg, Fe)O \cdot 3(Fe, Al)_2O_3 \cdot 10SiO_2+3H_2O$.
Schneider (1927):
$(K, Na)\,(Fe, Mg)\,(Fe, Al)_3 \cdot Si_6O_{18} \cdot 3H_2O$.
Hadding (1932):
$K_2O \cdot (Mg, Fe)O \cdot Fe_2O_3 \cdot Al_2O_3 \cdot 8SiO_2 \cdot 3H_2O$.
Gruner (1935):
$(OH)_{6-10} \cdot K_{2-3}(Mg, Fe'', Ca)_{1-3}(Fe''', Al, Si)_{3-6}(Si_{13-14}, Al_{2-3})O_{38-40}$.
Smulikowski (1936):
$H_4K(Mg, Fe'', Ca)\,(Al, Fe''')_3Si_6O_{20} \cdot 4H_2O$.

The writers agree with Gruner (1935, p. 705) that the various formulae suggested are all very close to the truth. Gruner's formula, however, appears to fit the existing analyses very well indeed and has a further advantage that it has been derived after consideration of the chemical composition and crystal structure of glauconite. Nevertheless Smulikowski's formula differs very little from that derived by *x*-ray analysis by Gruner. One of the analyses of New Zealand glauconite (No. 6) has been recalculated on the basis of 48 (O, OH) atoms to the unit cell and the derived formula fits Gruner's suggested formula reasonably well (Table VI). However, SiO_2 is rather higher than the theoretical figure 14. Nevertheless Gruner (1935, p. 713) points out that the excess of SiO_2 over Al_2O_3 gives rise to a higher Si:Al ratio in the $(Al, Si)_4O_{10}$ group than in mica, and that this might even result in substitution of a few Si ions for Fe''' or Al in positions with a covalency of 6. The writers considered it justifiable to use only 4% of $H_2O > 105$°C. in the calculation of the formula, after consideration of Ross's dehydration curve (1926, p. 8).

Table VI. Calculation of Formula of Glauconite (Anal. No. 6)

	Wt. %	mols.	48 (O, OH)		
SiO_2	47.42	0.790	14.444		14.444
Al_2O_3	7.19	0.070	2.558	2.000	2.000
				0.558	5.748
Fe_2O_3	22.64	0.142	5.190		
FeO	3.39	0.046	0.840		1.972
TiO_2	0.10	0.001	0.018		
CaO	0.27	0.004	0.072		
MgO	2.28	0.057	1.042		
K_2O	7.46	0.079	2.888		2.888
H_2O	4.00	0.222	8.116		8.116

Formula: $(OH)_{8.1}\cdot K_{2.8}\cdot (Mg, Fe'', Ca)_{1.9}\cdot (Fe''', Al)_{5.7}(Si_{14.4}, Al_2)O_{40}$.

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DIABOLEITE FROM MAMMOTH MINE, TIGER, ARIZONA

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In a paper published in 1938 on the "Geology and Ore Deposits of the Mammoth Mining Area, Pinal County, Arizona," N. B. Peterson included a description of the minerals found there by him up to that time and a discussion of their paragenesis and origin. To the long list of minerals given by Peterson, there may be added a number of rare species, some of which were previously known and others which have been brought to light by recent development of the mine. These minerals are under investigation at the University of Arizona and at Harvard University, and their complete description will, it is hoped, be published in the near future. At the present time one of them, diaboleite, which seems to be of peculiar interest, has been rather fully studied, and this paper is intended to present only the results of this study.

The materials under examination have been supplied to the Harvard Mineral Collection by Edwin Over, and we are under obligations to him for the opportunity to study so large a suite of specimens. Among them have been identified the following species not found in Peterson's list:—

- Atacamite
- Boleite
- Caledonite
- Diaboleite
- Embolite
- Matlockite
- Phosgenite
- Pseudoboleite?
- A mineral related to Hydrocerussite

Dioptase has been described in a paper by Galbraith and Kuhn (1940) of the University of Arizona.

Leadhillite is mentioned in Dana's *System of Mineralogy* on the authority of Penfield but without description. It is not uncommon in our specimens.

Linarite is briefly described by Guild (1910), but no idea is given there of its importance in the paragenesis of the Mammoth Mine minerals.

The last two minerals will be included in our future studies.

DIABOLEITE

The name diaboleite was proposed by L. J. Spencer (1923) for a new oxychloride of lead and copper found embedded in mendipite from the old, abandoned lead mines of the Mendip Hills, England. His material was scanty and the description was, therefore, incomplete; but it was sufficient to firmly establish the identity of the new species. It is a peculiar pleasure to be able to complete this description through the study of the abundant material found in the Mammoth Mine. It is also hoped that the more complete knowledge of this mineral and the intended study of members of the percylite-boleite group associated with it may clear up somewhat the perplexing relations between them.

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 244.

Diaboleite is tetragonal and hemimorphic. No general form is present so that from morphology alone the crystal class might be either tetragonal-pyramidal (wulfenite class) or ditetragonal-pyramidal. In the Weissenberg and Laue *x*-ray photographs, however, there are vertical planes of symmetry which prove it to belong to the latter class, $4mm$. This class has hitherto had no representative among minerals. Diaboleite is always in crystals which range from thin plates a mm. across to stout, stubby crystals up to 1.5 cm. in diameter. The platy habit dominates and, since crystals are usually attached to the cavity wall by an edge, the plates generally show in cross section the marked hemimorphic development.

The evidence of hemimorphism is of two sorts:—

(*a*) unlikeness of the upper and lower basal planes,
(*b*) unlikeness of pyramid development at the opposite ends of the vertical axis.

(*a*) The basal plane is smooth and reflecting in small crystals—more apt to be striated or replaced by vicinal pyramids in larger ones. It is rarely equally developed at both ends and the end of its larger development has been arbitrarily chosen as the lower or negative end. On many of the better, small crystals the negative pedion is relatively large and is smooth or marked by a square series of striae parallel to the axes, while the positive pedion is either lacking entirely or is a tiny square passing into a more or less curved vicinal second-order pyramid of low slope.

(*b*) The pyramids of diaboleite are of both the first and second orders. The first-order series is with rare exceptions confined to what has been chosen as the upper or positive extremity of the crystal. The second-order series is present on both terminations and is of more complex zonal development, always including the second-order prism.

Diaboleite crystals are of superb quality, the faces even when minute giving brilliant single reflections. Nine crystals were measured completely, each being set up twice to permit the study of both terminations. The unit cell was chosen in accordance with the *x*-ray study, detailed below, and angles of four forms, {101}, {201}, {111}, and {112} were employed in the calculation of the elements. The values are collected in Table 1, only faces giving perfect reflections being employed.

TABLE 1. DIABOLEITE: CALCULATION OF ELEMENT p_0

	No. of faces	ϕ	ρ	Range		p_0
				ϕ	ρ	
101	20	0°02′	43°07½′	0°00′– 0°07′	42°52′–43°18′	0.9366
201	20	0 02	61 54	0 00 – 0 04	61 47 –62 02	0.9364
112	20	44 55	33 28½	44 53 –45 00	33 22 –33 35	0.9352
111	9	44 58	52 56½	44 53 –45 00	52 52 –53 08	0.9364

The mean value of p_0 derived from the values of the last column is 0.9361, which is used in the calculation of the angles given in Table 2.

It is interesting to compare these results with what Spencer was able to observe on his poor and minute crystals. He reported $c\{001\}$, $a\{100\}$, $e\{101\}$ and $o\{307\}$. $a:c=1:0.95$, derived from the appoximate angle *ce* of 43½°. Spencer's {307} with *co* 22½° is probably our {102}, $cr=25°03'$.

TABLE 2. DIABOLEITE: ANGLE-TABLE

Tetragonal, ditetragonal-pyramidal 4*mm*.

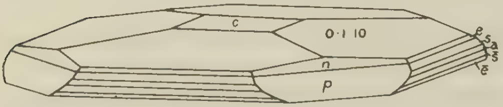
$c=p_0=0.9361$

Lower	Upper		ϕ	ρ	A	$\overline{M}$
$\bar{c}$	*c*	001	—	0°00′	90°00′	90°00′
	a	010	0°00′	90 00	90 00	135 00
	m	110	45 00	90 00	45 00	90 00
$\bar{r}$	*r*	012	0 00	25 05	90 00	72 33½
$\bar{e}$	*e*	011	0 00	43 06½	90 00	61 49
$\bar{s}$	*s*	021	0 00	61 53½	90 00	51 25
$\bar{n}$	*n*	112	45 00	33 30	67 01½	90 00
	p	111	45 00	52 56	55 39	90 00

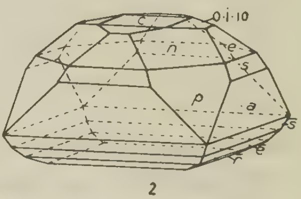
HABIT OF THE CRYSTALS

A tabular habit prevails and, as the crystals are attached by an edge, it is rare to find one complete. Very small ones, however, are nearly so and are often perfectly square tables or regular octagons in outline. The lower base is large and plane, generally bounded on the edges by narrow line faces of second-order pyramids and prisms. On but two of the very numerous crystals examined was there a trace of first-order pyramids on the lower end and then it was the form $\bar{n}\{11\bar{2}\}$.

The upper termination is apt to be dominated by the pyramid $n\{112\}$. This face or {111}, by impinging on the lower base, truncates the corners of the tablets to give the octagonal outline. Only exceptionally is the prism of the first order developed, but when it is the faces are as brilliant as are those of the more common second-order prism. Sometimes the polar edges of {112} are truncated symmetrically by narrow faces of {012}. More commonly, however, the upper termination consists in large



1



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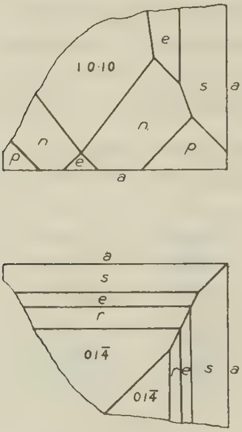

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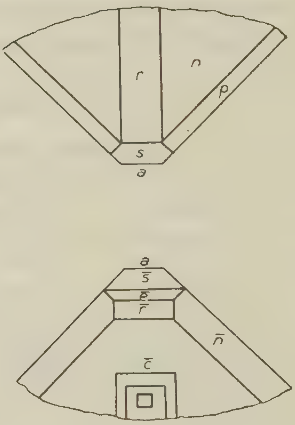

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FIG. 1. Crystal of diaboleite from Mammoth Mine. Above, $c\{001\}$, $a\{010\}$, a vicinal pyramid {0.1.10}, $e\{011\}$, $s\{021\}$, $n\{112\}$ and $p\{111\}$. Below $\bar{c}\{00\bar{1}\}$ dominant, $\bar{e}\{01\bar{1}\}$ and $\bar{s}\{02\bar{1}\}$. Commonest type.

FIG. 2. Crystal of diaboleite with forms similar to Figure 1 but much less tabular. A rare type.

FIG. 3. Plans of upper and lower ends of a thin tabular crystal of diaboleite, showing irregularity of quadratic pattern due to single vicinal faces.

FIG. 4. Plans of upper and lower ends of exceedingly thin tabular crystal of diaboleite showing marked hemimorphism, presence of the rare form $\bar{n}\{11\bar{2}\}$ and the square striation pattern on the lower pedion.

part of rounded faces of second-order pyramids of low inclination which are regarded as vicinal forms. Reflections from these faces are poor but seemed to group themselves about positions at angles to the base of about 5½°, 11½° and 13°. These angles correspond to forms as follows:—

	φ	ρ
1.0.10	0°00′	5°21′
209	0 00	11 45
104	0 00	13 10½

They are not regarded as definite forms, but not infrequently they are relatively large and on the larger crystals, where they are unequally developed, they cause the terminations to lose their usual quadratic symmetry. In the drawings they are shown only schematically.

The second-order pyramids of the upper ends of the crystals are three only; *r*, *e* and *s*. All are generally present on every crystal, although one or more may be line faces only. On the lower end the same three forms commonly occur but with them, or replacing one or more of them, other forms were found occasionally as shown below.

	No. of faces	Measured ρ	Calculated ρ
203	2	31°52′ 32 00	31°58′
302	4	54 25 54 07 54 39 54 13	54 32½
401	2	75 06 75 01	75 02½

These forms were never found on the upper termination. The vicinal forms described as belonging to the upper ends of the crystals are occasionally found replacing the lower base. It is not impossible that this is due to twinning, but no evidence could be secured to prove this. Otherwise, there is no evidence of any sort of twin relationship. The crystals often form subparallel aggregates or occur in quite irregular groups. There was no rule apparent as to attachment of the crystal by one or the other end of the polar axis; on the contrary, as has been stated, attachment is generally by an edge.

Diaboleite has a perfect and brilliant cleavage parallel to {001}, but it is not always easy to effect cleavage. The fracture transverse to the tables is conchoidal. Hardness 2½. Specific gravity 5.42 ± 0.01, determined on six separate, very pure crystal fragments on the Berman microbalance. This is much lower than the value given by Mountain (1923)—6.412,* which was determined on 0.1218 gram in the pycnometer; but is consistent with the chemistry and *x*-ray data here presented.

* It seems likely that this figure is due to a mistake in calculation, for the figures to the right of the decimal are in agreement.

The color of diaboleite is a very intense blue with a pale blue streak. It is noteworthy that there are in this series of minerals three others of almost the same deep blue color: azurite, a darker, less clear blue; linarite, not quite so intense and showing cleavage across the edges of the plates instead of parallel to them as in diaboleite; and boleite, which is in cubes with cubical cleavage and having a greenish tint, as compared with the diaboleite. In very thin plates there is sometimes a greenish tone to the blue color.

Optical Properties

Diaboleite is uniaxial negative, with some crystals showing a disturbance of the uniaxial cross, but this may be due to a subparallel aggregation. The irregularity of extinction typical of boleite is completely lacking in diaboleite. Under the microscope thick fragments are a deep blue with the absorption $\omega > \epsilon$ well marked (only in thick fragments). Refractive indices are $\omega = 1.98 \pm 0.01$, $\epsilon = 1.85 \pm 0.01$ (by the immersion method, using phosphorus-sulphur-methylene iodide liquids). The ω value is in agreement with Spencer's original measurement on a natural prism.

X-ray Crystallography

The *x*-ray diffraction study was made on a crystal with dimensions $.1 \times .4 \times .8$ mm. Rotation, 0-layer-line and 1-layer-line pictures were taken about each of the following rotation axes: [001], [100], and [110]. The pictures were very satisfactory for an accurate determination of the unit cell lengths and of the space group, since high-order reflections on the layer-line pictures showed unusually strong intensity. The constants for the unit cell derived from these pictures are:

$a_0 = 5.83 \pm 0.02$ $\quad V_0 = 185.58$ Å^3
$c_0 = 5.46 \pm 0.02$
$a_0 : c_0 = 1 : 0.937$
$a : c = 1 : 0.9361$ (Morph.)

The Laue symmetry group, derived from the presence of three symmetry planes and a 4-fold axis on the layer-line photographs, is $4/mmm$. All general order reflections are present, making the lattice primitive. No special operations are to be noted in the axial directions. Since morphological evidence shows clearly that the 4-fold axis is hemimorphic, the space group is fixed as $P4mm$.

Chemistry

The analysis of diaboleite made by Mr. F. A. Gonyer on the material from Mammoth Mine is in close agreement with that of Mountain in

Spencer and Mountain (1923) on the type material from the Mendip Hills. Both analyses are shown in Table 3. Using the analysis of Gonyer, recalculated to 100%, together with the specific gravity 5.42 and cell volume 185.58Å^3 determined in this study, we obtain the composition of the unit cell, which may be written $2Pb(OH)_2 \cdot CuCl_2$ (Spencer) or $Pb_2CuCl_2(OH)_4$. The derivation of this formula is shown in Table 3. The calculated density is 5.48 as compared with the measured 5.42. The one per cent deviation in these two values indicates the maximum deviation of composition, specific gravity and *x*-ray constants from the theoretical.

TABLE 3. COMPOSITION OF DIABOLEITE

	1	2	3		4	5
PbO	72.09	72.01	72.32	Pb	1.975	72.36
CuO	12.90	12.68	12.73	Cu	0.977	12.90
Cl_2	10.89	11.42	11.47	Cl	1.976	11.49
H_2O	6.14	6.03	6.06	H	4.114	5.84
Insol.	—	.19		O	4.011	
Total	102.02	102.33	102.58			102.59
Less $O=Cl_2$	2.46	2.57	2.58			2.59
	99.56	99.76	100.00			100.00

1. Diaboleite, Mendip Hills. Analysis by E. D. Mountain (1923).
2. Diaboleite, Mammoth Mine. Analysis by F. A. Gonyer on .9 gram.*
3. Analysis 2 recalculated to 100%.
4. Number of atoms in unit cell: volume = 185.58 Å^3; $d=5.42$, $M_0=609.68$.
5. Calculated composition for $Pb_2CuCl_2(OH)_4$.

RELATIONS TO OTHER MINERALS

Counting fragments large and small, several hundred specimens containing diaboleite are at hand in the collection. In the vast majority of them there is no other mineral except quartz and hemimorphite.

The author had the opportunity of making a brief examination of the 500-foot level of the mine, in June 1941, in the company of F. W. Galbraith and by the courtesy of the Mine Manager, Mr. Fozard. Although permitting but a glimpse of the deposit, the visit made it certain that the mineral diaboleite is widely distributed in the Collins Vein of the Mammoth Mine in the 400- and 500-foot levels at least. It occurs with linarite, for which it has been commonly mistaken.

Until more work is done on the general paragenesis it is not possible to place diaboleite accurately in the Mammoth Mine mineral sequence.

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* Spectrographic analysis shows presence of Ca, Si, Cr, Fe, in small amounts (less than 0.1%), and Al, Ba, Zn, Mg, Ti in less amounts.

It is, in general, a late mineral, often found in drusy cavities of quartz. With it are commonly to be found cerussite and wulfenite; more rarely dioptase, and implanted upon it are crystals of boleite, pseudoboleite (?) and quartz. In one specimen diaboleite is cut by a tiny vein of hemimorphite, and spherules of needles of this mineral are implanted upon it. The green minerals associated with it have not yet been examined, nor have various acicular white minerals of high luster. Intergrowths of diaboleite and phosgenite were noted which indicated a replacement, but which is the older has not yet been determined. In some cases diaboleite is altered to an aggregate of lighter blue material, but as yet the nature of this product has not been established.

The author desires to state that his part in the study of diaboleite is confined to the crystallography. Dr. Berman measured the optical constants and the specific gravity. The *x*-ray study was made by C. W. Wolfe. The chemical analysis is the work of F. A. Gonyer.

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VALENTINITE CRYSTALS FROM CALIFORNIA

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Abstract

Valentinite crystals from Lone Tree Canyon, Kern County, California, show an unusual habit. The individuals are lathlike in habit, bounded by a broad and elongated base, a narrow side pinacoid, and a series of eighteen prisms, many of which are line faces. No pyramids or domes are present. New forms are the prisms $\{560\}$, $\{670\}$, $\{12.11.0\}$, $\{870\}$, $\{970\}$, and $\{750\}$.

Valentinite Crystals from California

Valentinite, the orthorhombic form of Sb_2O_3, is common as an alteration product of stibnite, but is rather rarely crystallized. Accordingly, any occurrence as crystals is worth recording, and the more so in the present instance, as the crystals appear in a habit hitherto not reported.

The mineral has been previously reported from two California localities, once as poor, unterminated crystals from Kern County,[1] and once as pseudomorphs after stibnite, from San Benito County.[2] Undoubtedly it is commonly present as an alteration product of stibnite in many other localities, but not differentiated from other similar oxides, such as cervantite, stibiconite, etc.

A specimen of partly oxidized stibnite, collected by the writer from one of the small antimony mines in Lone Tree Canyon, Kern County, California, was found to have several small vugs lined with valentinite crystals. These crystals are small, the largest measuring approximately $1\times0.25\times0.1$ mm., and elongated tabular in habit, attached to the matrix by one end. The faces present are $c\{001\}$, $b\{010\}$ and a numerous series of prisms to be described more fully; *c* is ordinarily the largest, and nearly always whitened, or roughened, so that it gives a poor reflection. Next in size is *b*, usually long and narrow, and also of very poor quality. The prism faces are all smooth and shiny, and where wide enough, give good signals on the goniometer. Many of them, however, are narrow or line faces, and the signals are poor, or merge into a more or less continuous train, in which the brighter spots cannot always be determined with certainty. One notable peculiarity of the crystals is that the prisms, which form the terminations of the crystals, often do not appear symmetrically. Thus, there may be present on a crystal the forms: $\{110\}$, $\{760\}$, $\{7\bar{6}0\}$, $\{8\bar{9}0\}$, or $\{110\}$, $\{5\bar{4}0\}$, $\{4\bar{3}0\}$, $\{10.\bar{7}.0\}$, and $\{14.\bar{9}.0\}$. This lack of balance, and the roughness of *b* makes it sometimes difficult to orient the crystals accurately with respect to true position. In addition, there is a frequent tendency for the side pinacoids to diverge from parallelism, this divergence being in one instance as much as 4°, although usually it is less than $\frac{1}{2}$°. This is apparently not due to subparallel groups, as optically such crystals are single individuals. The general habit of this valentinite is shown in Fig. 1. A few crystals showed the suggestion of poor reflections in the [0*kl*] zone at a small angle from {001}, but these were so vague that they could not be considered as representing faces. No pyramid faces were noted on any crystal.

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[1] Behre, C. H., Jr., Native antimony from Kern County: *Am. Jour. Sci.*, 5th Series, **2**, 330–331 (1921).

[2] Rogers, A. F., Notes on rare minerals from California: *School of Mines Quart.*, **33**, 373 (1932).

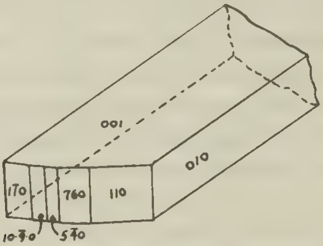

FIG. 1

This habit for valentinite appears to be most unusual, as the recorded habits all show domes or pyramids with the prisms. Crystals from Bräunsdorf show prism and brachydome, either nearly equidimensional, or elongated parallel to *a*, or are tabular parallel to {010}.[3] From Ballao, Italy,[4] considerably elongated parallel to *b*, with {110}, and a flat pyramid {5.10.8} strongly developed, so that the crystals are sharply pointed. From Bolivia[5] the crystals are tabular parallel to *b*. From Crook County, Oregon,[6] the crystals are slender prismatic parallel to *c*, with a brachydome and a complex series of prisms. From Sensa, Algeria,[7] minute crystals are reported, slender prismatic parallel to *c*, with prisms, domes, and many pyramids.

Because of this unusual habit, considerable hesitation was felt in identifying the mineral as valentinite. However, all the other physical, chemical, and optical properties agree with those of valentinite, and in addition, *x*-ray measurements kindly made for the writer by Dr. J. D. McCullough of the Department of Chemistry, University of California

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[3] Hintze, C., *Handbuch der Mineralogie*, **1**, pt. 2, p. 1238.

[4] Cavatino, A., Valentinite della Miniera di Ballao: *R. Acad. Naz. Lincei, Atti. Rend.*, Ser. 6, **25**, f. 3, 140–144 (1937).

[5] Spencer, L. J., On some Bolivian minerals: *Mineral. Mag.*, **14**, 328 (1907).

[6] Schaller, W. T., Crystallography of valentinite: *Am. Mineral.*, **22**, 652–662 (1937).

[7] Ungemach, M. H., Sur la Valentinite: *Bull. soc. franc. mineral.*, **35**, 539–552 (1912).

(Los Angeles), check closely with those determined by Buerger and Hendricks,[8] so that its identity may be considered settled.

The crystals are orthorhombic, and show a perfect cleavage parallel to a prism of 42°40′ [$m\wedge m'''$ for valentinite is 42°41′] as measured on the goniometer. The luster is vitreous to adamantine, $H=2\pm$, and the fusibility is very low. The mineral heated in a closed tube fused readily and gave off no water, but formed a sublimate of minute white octahedra.

TABLE 1

New forms are starred

Form		Times observed	Average reading	Variations	Calculated
*	560	2	64°42′		64°42′
*	670	1	65°16′		65°19′
*	780	2	65°47′		65°46′
*	890	7	66°33′	(66°00′–67°20′)	66°11′
m	110	15	68°34′	(67°28′–69°32′)	68°30′
*	12.11.0	6	69°39′	(69°20′–70°00′)	70°09′
D	10.9.0	5	70°25′	(70°08′–70°46′)	70°29′
*	870	2	70°48′		70°59′
E	760	12	71°25′	(71°00′–72°00′)	71°21′
σ	540	10	72°35′	(72°12′–72°44′)	72°31′
*	970	5	72°57′	(72°50′–73°12′)	72°58′
F	430	15	73°32′	(73°14′–73°52′)	73°33′
*	750	5	74°07′	(73°58′–74°20′)	74°17′
G	10.7.0	10	74°40′	(74°25′–74°50′)	74°35′
H	14.9.0	9	75°32′	(75°12′–75°56′)	75°48′
J	530	8	76°43′	(76°24′–77°08′)	76°42′
K	950	3	77°56′		77°40′
M	210	6	78°44′	(78°24′–79°28′)	78°52′

The amount of material available was too small for quantitative analysis, but qualitative microchemical tests showed only antimony. The color when pure is faint honey-yellow to colorless, but the crystals may be coated with a white opaque crust, or colored unevenly red by a stain, possibly kermesite.

Optically, the mineral is negative, shows parallel extinction, a very high index (not measured, but far above 1.73), and cleavage flakes show an off-center acute bisectrix figure. Dispersion is high with $r<v$, and crossed, with the optic plane parallel to {001} for blue, and to {100} for red. Because of the extremely high index and dispersion, 2V was not measured accurately, but is about 25° for blue and 10° for red. No twinning was observed.

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[8] Buerger, M. J., and Hendricks, S. B., The crystal structure of valentinite: *Zeits. Krist.*, **98**, 1–30 (1937).

The prism zone presents a complex series of forms ranging from {120} to {410}, including a number of the forms recently found by Schaller[9] and eight new ones. These forms, with the number of times each occurs, the average observed angles, and calculated angles, are shown in Table 1. Owing to the difficulty, as noted above, in orienting the crystals, some of these forms may be somewhat doubtful, but in general, agreement with calculated values is reasonably close.

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[9] Schaller, *op. cit.*, p. 654.

A. C. GILL'S DEVELOPMENT OF THE CONCEPT OF UNIQUE DIAMETERS IN CRYSTALLOGRAPHY

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ABSTRACT

A unique diameter is a line, or diameter, unlike any other in the crystal. All parallel lines are the same line crystallographically. Some properties, physical, chemical, and/or crystallographic, along a unique diameter are different from those along any other line in the crystal.

Several criteria based on physical and chemical properties, the groupings of faces and angles between faces, and the dimensions of crystals may be used to recognize unique diameters. Likewise, laws controlling their distribution in crystals and their relations to the various elements of symmetry may be formulated. Since their arrangement in each crystal system is different from that in any other, except that the tetragonal and hexagonal are alike, unique diameters, in conjunction with like diameters, may be used to define the six crystal systems independent of symmetry and axes of reference, and the selection and orientation of axes of reference may be based on them and certain like diameters.

Some of the applications and relationships of this concept are: (1) the assignment of crystals to systems without the use of symmetry or hypothetical axes of reference; (2) the easy selection of axes of reference; (3) the determination of the crystal system to which a mineral belongs from its cleavage fragment; (4) a clarification of some of the relationships and conditions observed in optical mineralogy; and (5) the simplification of the teaching of crystallography, especially in short courses where it is desirable to present only the commoner forms and not to discuss classes.

This concept presents a basis for the definition and treatment of systems founded on inherent, independent properties and not on hypothetical axes of reference nor on groupings of classes.

INTRODUCTION

The origin of the concept of unique diameters is somewhat obscure. However, the material here presented is substantially that used for many years by the late Professor A. C. Gill in his successful teaching of crystallography at Cornell University. According to statements made by Professor Gill,[1] the idea originated with some German crystallographer, who is reported to have published a note on the subject during the latter part of the last century. Professor Gill obtained the basic germ of the concept from the above-mentioned German crystallographer either by personal communication or from his published note and developed it into a logical sequence of ideas. The material in the form presented in this paper is substantially that developed by Professor Gill and used by him in his lectures on crystallography. In all his considerations of crystals, Professor Gill emphasized the significance of this method, and it was under his instruction that the writer obtained his knowledge of the concept.

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[1] Dr. Evans B. Mayo, personal communication, the writer, and others. However, Drs. Hermann F. Vieweg and James H. C. Martens, who were also closely associated with Dr. Gill, and a few others, have no recollection of his crediting the conception of the idea to another person.

As no trace of the original notice, if any existed, has been located and since this material in its current form has never been published, it seems desirable to present it at this time.

DEFINITIONS

In any crystal structure, either any line, or diameter, must be unique or there must be others like it in all respects. *A unique diameter, then, is a line different from any other in the crystal.* Examples of unique diameters are the "*c*" axes in the tetragonal and in the hexagonal systems and the three axes of reference in the orthorhombic system.

Like lines, or diameters, are lines which are identical in all respects. The two lateral axes of crystals in the tetragonal system are like lines, as are the three lateral axes of those in the hexagonal system. Every line in crystals of the isometric system has two or more lines like it.

Along every line, whether unique or not, there are two directions, which are opposed to each other in sense. These directions may or may not be alike. A sphere of quartz partially dissolved by hydrofluoric acid[2] is a case in point. The two directions along the "*c*" axis of reference are alike; therefore, the two ends of this axis are attacked in the same manner. On the other hand, the opposing directions along each of the lateral axes of reference are unlike; therefore, the positive and the negative ends of these axes are differently affected in such a manner that the negative end of any axis is appreciably dissolved, whereas the positive end is only slightly (much less) affected.

All parallel lines in a crystal are considered to be the same (one) line, all parallel planes to be the same (one) plane, and all parallel directions to be the same (one) direction if taken in the same sense. These parallel lines, planes, or directions are alike in every respect.[3] Therefore, the use of the term "diameter" as synonymous with "line" is justified, since, in any set of parallel lines (which is considered as a single line), there is always one which passes through the center of the crystal.

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[2] Penfield, S. L., and Meyer, Otto, Results obtained by etching a sphere and crystals of quartz with hydrofluoric acid: *Conn. Ac., Tr.* **8,** 158–165 (1890); *Yale Bicen. Pub., Contr. Min.,* 160–167 (1901).

Gill, A. Capen, Beiträge zur Kenntniss des Quarzes: *Zeits. Kryst.,* **22,** Bd. 2, 3–34 (1893).

Dana, E. S., *Textbook of Mineralogy,* 4th ed. by W. E. Ford, John Wiley and Sons, New York, **1932,** p. 213.

[3] The writer is aware of the fact that, in the atomic structure of minerals, the planes formed by sheets of atoms are different from the planes in space lying between these sheets of atoms. Likewise, the lines formed by rows of atoms are not like the lines in space between these rows of atoms. Furthermore, in the atomic structure of many minerals, adjacent rows or sheets of atoms themselves are different. However, when the largest unit which does not contain a repetition is taken, it is repeated indefinitely throughout the structure and accordingly similar properties result, such as repeated potential planes of cleavage be-

Some properties, physical or chemical, along or at the ends of a unique diameter must be different from those along or at the ends of any other diameter in the crystal. This shows that the atomic structure along a unique diameter is different from that along any other line in the crystal.

All like planes, lines, or directions in a crystal must be alike in every respect. Therefore, all properties, physical and chemical, manifested by one plane, line, or direction must be shown in like degree by all like planes, lines, or directions. The atomic structure of like planes, lines, or directions is identical.

Physical properties of unique and like lines (and the planes perpendicular to these lines) are well illustrated in gypsum. Crystals of this mineral have a plane in which all diameters are unique, the plane parallel to *b*{010}, and one, and only one, other unique diameter, the normal to this plane. On *b*{010}, which is perpendicular to the single unique diameter, there is perfect cleavage, pearly luster, and a hardness of 2; whereas, on *a*{100}, which is normal to a unique diameter of the plane of unique diameters, there is imperfect cleavage yielding a conchoidal surface, vitreous luster, and a higher hardness. These assemblages of physical properties are peculiar to the faces mentioned. However, the $\{\bar{1}11\}$ cleavage is perpendicular to two diameters which are alike, and, while having properties different from the two cleavages mentioned above, has two directions of cleavage, which are alike in their properties. Other excellent examples of like properties exhibited by faces perpendicular to like directions (like faces) are seen in galena, halite, sphalerite, hornblende, etc. Hornblende also illustrates different properties of different diameters.

Chemical properties of unique and like lines are well illustrated by the corroded quartz sphere previously mentioned.[4] Such a sphere is attacked rapidly in the direction of the unique diameter, the "*c*" axis of reference, to a degree different from that along any other line in the crystal. At the positive extremities of the lateral axes of reference, the crystal is attacked very slowly, but in a similar manner at each positive extremity (like directions). Likewise, the negative extremities of the lateral axes of reference are attacked in a manner similar to one another but different from and greater than the positive ends, yet less than the attack at the ends of the "*c*" axis.

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tween adjacent planar units (one plane) and similar behavior of light along parallel linear units (one line). The former is commonly spoken of as *a single* direction of cleavage.

[4] Penfield, S. L., and Meyer, Otto, *op. cit.* Gill, A. C., *op. cit.* Dana, E. S., 4th ed. by W. E. Ford, *op. cit.*

CRITERIA OF UNIQUE DIAMETERS

The following criteria may be used in recognizing unique diameters:

1. The dimensions of the crystal not equal,—some longer or shorter than others.

An example of this is the greater or less length of the "*c*" axes of tetragonal and hexagonal crystals in comparison with the lateral axes.

This criterion must, of course, be used with extreme care in dealing with actual crystals, because of malformation, but it is suggestive in use with wooden models and to a much less extent with actual crystals themselves. It should, however, always be verified with one of the following criteria.

2. Groupings of faces and angles between faces around the ends of or in relation to one line different from all others.

Examples of this may be seen in tetragonal and hexagonal combinations of prisms and bipyramids. In these systems the "*c*" axes are the unique diameters.

This criterion is the most serviceable for quick determination in all ordinary work.

3. Chemical and physical properties along or at the ends of one line different from those along or at the ends of any other line.

Again the quartz sphere referred to above[4] may be used as an example. Solution along the "*c*" axis, or unique diameter, was considerably more pronounced than along any other line in the crystal.

The behavior of light along the "*c*" axes, or unique diameters, of tetragonal and hexagonal crystals is an example of physical properties along unique diameters being different from those along any other lines in the crystal.

DISTRIBUTIONS OF UNIQUE DIAMETERS IN CRYSTALS

The distributions of unique diameters in crystals are subject to the following restrictions:

1. If two diameters are unique and at right angles to each other, then in their plane either all diameters are unique or these are the only two; but, in either case, the line perpendicular to their plane must be unique.

Crystals in the orthorhombic system, in which the three axes of reference are the unique diameters, serve as examples in the latter case (in which the two unique diameters are the only two in their plane). In the former (in which all diameters in their plane are unique), crystals in the monoclinic system may be used, since the plane of the axes "*a*" and "*c*" is a plane of unique diameters and the axis "*b*" is unique. In the plane of unique diameters, any two such lines at right angles to each other may be selected to fulfill the conditions of this case.

2. If two diameters are unique and oblique to each other, all diameters in their plane are unique and also the line normal to their plane.

Crystals in the monoclinic system may again be used as an example, since the plane of the axes of reference "*a*" and "*c*" is a plane of unique diameters as is the line normal to this plane. Here, however, two unique diameters oblique to each other, such as the axes "*a*" and "*c*," may be selected to fulfill the conditions of the case.

3. If there is a plane of unique diameters, and, in addition to the unique line normal to this plane, which must necessarily be present, there exists still another unique line, then all diameters in the crystals must be unique.

The triclinic system serves as an example of this case. In this system all diameters are unique. However, we may select a plane, which will be a plane of unique diameters, and a normal to this plane, which will also be unique. Then any other line selected in the crystal will be unique, and all lines in the crystal are unique.

The monoclinic system offers the reverse of this. There is a plane of unique diameters, the plane of the axes of reference "*a*" and "*c*," and there is a unique line normal to this plane, the axis "*b*." However, any line other than these lines has another line like it in the crystal, and these diameters are, therefore, the only unique ones present.

4. If there is a plane of symmetry, all unique diameters must lie in this plane or be perpendicular to it. No unique direction can be normal to a plane of symmetry. Unique directions may, however, lie in the plane of symmetry.

The plane of symmetry of the monoclinic system illustrates this case, since it is coincident with the plane of unique diameters and there is a unique diameter normal to it but nowhere else.

The tetragonal and hexagonal systems also illustrate this case, since all planes of symmetry either include or are normal to the "*c*" axis, or unique diameter.

No unique direction can be normal to a plane of symmetry, because a direction on one side of the plane will be repeated on the other side in opposite sense and will, therefore, not be unique. However, those directions lying in the plane of symmetry are not repeated by it and may, therefore, be unique. In the mineral hemimorphite, the two orthorhombic axes "*a*" and "*b*" are unique lines and are normal to planes of symmetry. The opposing directions along each of these axes are alike. However, along the vertical axis "*c*," which is also unique but which is not perpendicular to a plane of symmetry, the opposing directions are unique.

5. If there is a 180° axis of symmetry, all unique diameters must be coincident with or normal to this axis. No unique direction can be normal

to a 180° axis of symmetry. Two such directions may, however, be coincident with such an axis.

Orthorhombic and monoclinic crystals illustrate this case—as do tetragonal and hexagonal ones also. In orthorhombic crystals, the axes of reference being the unique diameters and, in one case or another, axes of symmetry, these axes are always coincident with or normal to a 180° axis of symmetry.

In monoclinic crystals, the "*b*" axis may or may not be an axis of symmetry, but no other line can be in this system. However, when it is, since it and the plane normal to it are unique, all unique diameters are either coincident with or normal to this axis.

The mineral hemimorphite illustrates the latter part of this case. This mineral belongs to the hemimorphic class, which is characterized by two planes of symmetry with a 180° axis of symmetry at their intersection, the latter being the "*c*" axis of reference. In crystals of this mineral, the "*a*" and "*b*" axes are unique lines, and the two opposing directions along them and normal to the 180° axis of symmetry are alike. On the other hand, the "*c*" axis, or axis of symmetry, is a unique line, but the two directions on this line are unique also and, therefore, coincident with a 180° axis of symmetry.

6. If there is a 120°, a 90°, or a 60° axis of symmetry, it may or may not be unique, but no other diameter in the crystal can be. (Regarding a 60° axis, this statement concerns only the restrictions imposed by the axis itself.)

In the isometric system 120° and 90° axes of symmetry can be found which are not unique, and no other line in the crystal is unique. No 60° axis of symmetry which is not unique occurs in crystals.

In the tetragonal and hexagonal systems, 90° and 60° (or 120°) axes of symmetry, respectively, may be found. These lines are unique, but no other is in these crystals.

7. A center of symmetry imposes no limitations on unique diameters. However, if there is a center of symmetry, there can be no unique directions in the crystal, for every direction is like its opposite.

The triclinic system, in which all diameters are unique, is an illustration. In the normal, or pinacoidal class, which has only a center of symmetry, all lines are unique, but no directions are, hence the forms are all two-faced forms, or pinacoids. On the other hand, in the hemihedral, or pedial class, which has no symmetry at all, all lines, as well as all directions, are unique, hence the forms are one-faced forms, pedions.

Possible Arrangements of Unique Diameters in Crystals

Unique diameters have the following arrangements in crystals and no others:

1. No diameters unique.
2. One unique diameter.
3. Three, and only three, unique diameters at right angles to one another.
4. All diameters in one plane unique and only one other unique diameter, which is normal to this plane.
5. All diameters unique.

Definitions of the Six Crystal Systems in Terms of Unique and Like Diameters

1. The isometric system has no unique diameters. It has, among others, three like diameters at right angles to one another.
2. The tetragonal system has one, and only one, unique diameter; and, in the plane normal to it, any two diameters at right angles to each other are alike.
3. The hexagonal system has one, and only one, unique diameter; and, in the plane normal to it, any three diameters at 120° with one another are alike.
4. The orthorhombic system has three, and only three, unique diameters, which are at right angles to one another.
5. The monoclinic system has one plane in which all diameters are unique, and only one other unique diameter; namely, the normal to this plane.
6. The triclinic system has all diameters unique.

Selection of Axes of Reference and Orientation of Crystals for Description by Means of Unique and Like Diameters

1. *Isometric system.* The three like lines at right angles to one another are chosen as the axes of reference. There is only one such possibility.

2. *Tetragonal system.* The unique diameter is set as the vertical axis, the "*c*" axis. In the plane at right angles to this unique diameter, two important like lines perpendicular to each other (axes of symmetry, if possible) are chosen as the lateral, or "*a*," axes.

3. *Hexagonal system.* The unique diameter is set as the vertical axis, the "*c*" axis. In the plane normal to this unique diameter, three prominent like lines at 120° to one another (axes of symmetry, if feasible) are selected as the lateral, or "*a*," axes.

4. *Orthorhombic system.* The three unique diameters are chosen as the axes of reference. One of these (the most convenient) is set vertically and designated by the letter "*c*." The longer of the other two is set right and left, designated by the letter "*b*," and called the macro-axis. The shorter of the lateral axes is then front and back, is designated by the letter "*a*," and is called the brachy-axis.

5. *Monoclinic system.* The plane of unique diameters is set vertically and front and back. The unique line perpendicular to this plane is, therefore, right and left, is designated by the letter "*b*," and is called the ortho-axis. In the plane of unique diameters, a prominent line (the most convenient) is selected, set vertically, and designated by the letter "*c*." Another such line, in general at oblique angles to "*c*," is set sloping downward toward the observer, designated by the letter "*a*," and called the clino-axis.

6. *Triclinic system.* Three prominent lines are chosen as the axes of reference. Lines which give the simplest relations in description are chosen. These are commonly axes of prominent zones. One of these axes (the most convenient) is set in a vertical position and designated by the letter "*c*." The longer of the other two is usually set right and left and sloping downward toward the right, if feasible, designated by the letter "*b*," and called the macro-axis. The third, then falls in a general front-back position, is designated by the letter "*a*," and is called the brachy-axis.

APPLICATIONS OF THE CONCEPT

1. By using this concept, crystals can be assigned to systems without reference to symmetry or to hypothetical axes of reference.

2. The crystal system to which a mineral belongs can often be determined from cleavage fragments of the mineral. In many cases, where the specific crystal system cannot be determined, the mineral can be narrowed down to one of several systems without the use of symmetry.

For example, in studying a cleavage fragment of selenite, it can be seen that there are two unique diameters oblique to each other, one normal to the $\{100\}$ cleavage and one bisecting the angle of the $\{\bar{1}11\}$ cleavage and lying in $\{010\}$. These lines are unique, since each of these cleavages manifests properties different from those of any other plane in the crystal. In the latter cleavage, the line bisecting the angle between the cleavage surfaces and lying in the plane of $\{010\}$ must be unique, because there are no others like it in the crystal. Since these two unique diameters are oblique to each other, they must lie in a plane of unique lines, in accordance with the second case of distribution of unique diameters. The $\{010\}$ cleavage lies in this plane and, for reasons similar to those cited above, is perpendicular to a unique diameter. This arrangement, a plane of unique diameters and a unique diameter perpendicular to this plane, fulfills conditions found in the monoclinic and the triclinic systems. However, this crystal must belong to the monoclinic system, because of the $\{\bar{1}11\}$ cleavage, which is parallel to a four-faced form and, therefore, cannot be triclinic and because every line other than those in the plane of unique diameters and the one normal to this plane is, and can be seen to be, like some other line in the crystal, a condition found only in monoclinic crystals.

One other example might be cited. In a cleavage fragment of hornblende, the line of intersection of the cleavage surfaces is unique, as are the two lines bisecting the angles between the cleavage surfaces and lying in the plane perpendicular to them. There can be determined, then, from such a fragment three unique lines at right angles to one another. Such a fragment must be, from these data, in either the orthorhombic or the monoclinic systems; for the two like directions of cleavage exclude the triclinic and the absence of a face cutting the "*c*" axis makes it impossible to distinguish between these two systems.

3. If unique diameters are lines each of which has some properties different from those of any other line in a crystal, it follows that optical properties are likely to be greatly influenced by them. This is found to be the case. In the isometric system, which has no unique diameters, the optical indicatrix is a sphere. In tetragonal and hexagonal crystals, the "ϵ" axis of the optical indicatrix coincides with the single unique diameter. This optical indicatrix is an ellipsoid of revolution, and the "ϵ" axis is a unique axis. In orthorhombic crystals, the principal axes of the optical indicatrix coincide with the three unique diameters. The principal axes of the indicatrix for biaxial crystals are themselves unique. In the monoclinic system, two such principal axes lie in the plane of unique diameters and the third coincides with the unique diameter which is normal to this plane. In the triclinic system since all diameters are unique, there is no set relationship between crystallographic and optical directions; the principal axes of the optical indicatrix can coincide with any three unique diameters at right angles to one another.

4. Similarly, in a consideration of the atomic structure of crystals, certain rows of atoms can be seen to be unique and certain rows have others like them. In fact, the term "unique rows of atoms" has been used by some *x*-ray specialists in discussing the atomic structure of minerals.

5. This concept can be used to advantage in a short course in mineralogy—a one semester course, for example—where the amount of time available does not warrant a discussion of classes. Systems can then be defined in terms of unique diameters, and the commonest forms in the several systems described without reference to classes other than a discussion of symmetry and a statement of the basis on which the division of crystals into classes is made. Crystallography then is a complete, integral unit to the student, and this method avoids the feeling on his part of having covered only certain specific sections of the subject.

This method of treatment can also be used in longer courses in which all or many of the classes are discussed; and, in this application, it presents a simple, direct, real approach to systems.

SUMMARY

This concept presents a basis for the definition and treatment of systems founded on inherent, independent properties and not on hypothetical axes of reference, nor on groupings of classes.

ACKNOWLEDGMENTS

The writer desires to express his sincere appreciation to Dr. Evans B. Mayo, who has offered many valuable suggestions in the course of the preparation of this paper. He also would like to thank Mr. John Rodgers, Dr. Hermann F. Vieweg, Dr. J. H. C. Martens, and members of the Department of Geology of Cornell University, who have read all or parts of the manuscript and offered pertinent criticisms.

NOTES AND NEWS

SEDIMENTARY ANALCITE*

Clarence S. Ross, *U. S. Geological Survey, Washington, D. C.*

Analcite from sedimentary beds was described from two widely separated localities in 1928,[1] one from Utah, Colorado, and Wyoming; and the other from near Wikieup, Arizona.[2] Bradley stated, "Field and microscopic study of these two types of zeolite-bearing rocks indicates that both minerals [analcite and apophyllite] formed in place on the lake bottom (or when only shallowly buried in ooze) as a result of interaction between various salts dissolved in the lake water and the dissolution products of volcanic ash that fell into the ancient Green River lakes."

The Arizona material was submitted for identification by a local collector and no field examination was possible at the time. This did not permit definite conclusions on origin, but Ross made the following suggestion, " . . . volcanic ash showers frequently deposited beds of glassy ash in these playa lakes. Material of this kind commonly alters to bentonite but in the presence of concentrated sodium salts it might form analcite."

The origin of this material presented an interesting problem and Bernard Moore was requested to collect additional material during field work in 1934, while taking part in the study of the mineral resources of the region around Boulder Dam.

Mr. Moore submitted the following geologic section:

Geologic Section near Wikieup on Big Sandy-Burro Creek, Arizona

Green arkosic sand	20 feet
Brown clay	30 feet
Porous tufa	1 foot
Green sands	2–3 feet
Brown clay	25 feet
Limy sand	1 foot
Green analcite	6–12 inches
Brown clay	

The following descriptions are based on studies of the material collected by Moore.

The green analcite is the material first recognized as analcite. It has a dull gray-green color, due to a thin film of nontronite clay between the grains of analcite that average 0.05 millimeters in diameter. Most of the grains are roughly rounded but some of these show euhedral outlines. These grains are cemented into a fairly coherent sandstone-like rock, with

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[1] Bradley, W. H., Zeolite beds in the Green River formation: *Science*, **67**, 73–74 (1928).

[2] Ross, Clarence S., Sedimentary analcite: *Am. Mineral.*, **13**, 195–197 (1928).

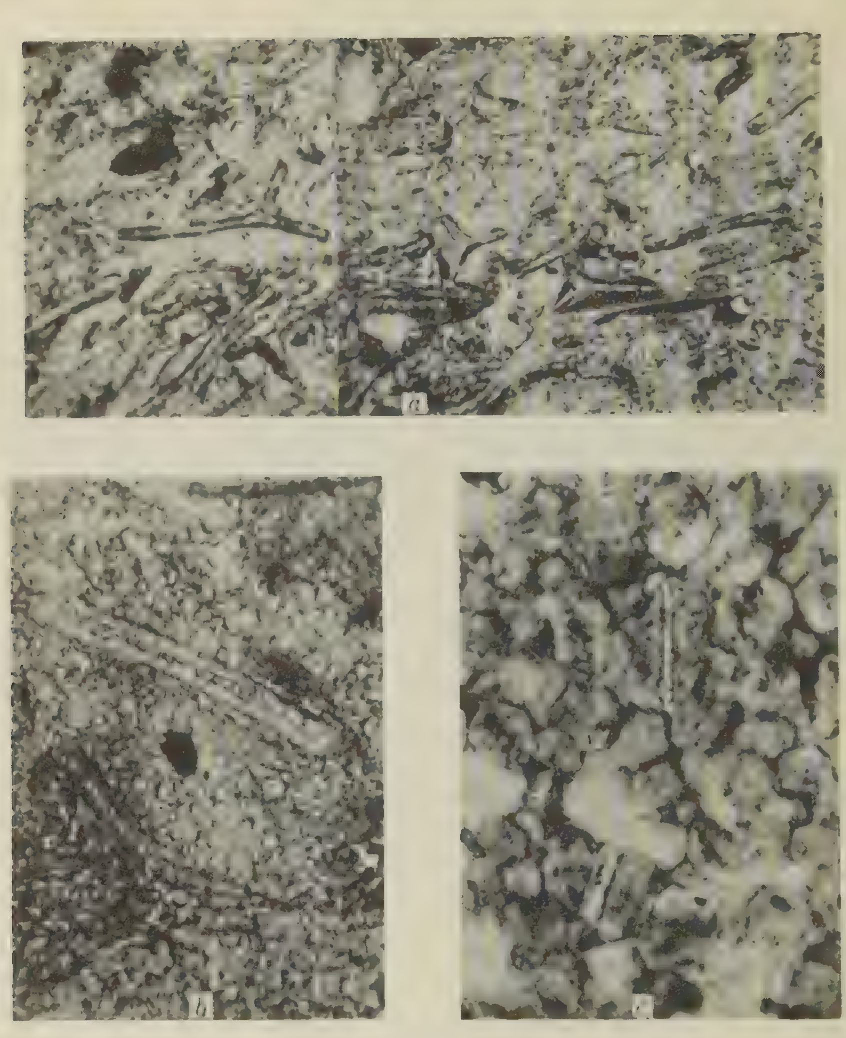

PLATE 1

Illustrating volcanic ash structure in analcite rock from near Wikieup, Arizona

Figure *a*. The lath and Y-shaped structures are typical volcanic glass shards, but have been completely altered to analcite. Interstitial material is also analcite grains, many of them showing hexagonal outline. ×65.

Figure *b*. Shards showing double row of analcite grains. ×100.

Figure *c*. Coarse-grained nearly pure analcite rock showing two platy shard structures, cutting through a single analcite grain. Dark material is pigmenting grains of iron-rich clay. ×54.

about 25 per cent of pore space. The tuff structure is not well preserved, but traces of it are shown in plate 1, Fig. *c*.

The "porous tufa" is a nearly white, fine-grained tuff-like material. Microscopic study indicated that it, like the green material, was composed essentially of analcite. Here, however, the tuff structure is perfectly preserved as shown in plate 1, Fig. *a*. Most of the original shards were flattened or slightly curved plates of glass, but many have the Y-shapes that are formed at the juncture of three bubbles. A few unbroken spherical bubbles are preserved. The fragments range up to about 0.5 millimeters in length and have been altered to analcite, together with perhaps about 20 per cent of bentonitic clay. The analcite grains range from 0.003 to 0.015 mm. in diameter, are colorless, and roughly euhedral in outline. Commonly a double row of analcite grains have formed within an altered shard as shown in plate 1, Fig. *b*. The clay material is slightly brownish. Orthoclase, biotite, and hornblende grains commonly represent less than 1 per cent of the material, but a few narrow lenses contain a little detrital quartz and small rounded oolite-like grains of carbonate are present.

Thus the Wikieup analcite was obviously derived from glassy volcanic ash. Moore concluded that the material was deposited in a playa; and there seems little doubt that sodium salts were the factor that resulted in analcite rather than bentonite, the normal product when glassy volcanic ash breaks down.

SHORTITE: CORRECTION OF SPACE GROUP[a]

W. E. Richmond, *Geological Survey, Washington, D. C.*

The space group of shortite was previously determined by the writer[1] to be D_2^6-$A222$. This choice of space group was based on the reflections given below, all of which were not given in the original paper. These reflections lead to the "probable" space group D_2^6-$A222$, as given in the *International Tables.*[2]

The reflections obtained from zero and first layer-line photographs about [100] and a zero layer-line photograph about [010] are listed below.

$hkl = k+l$ even
$0kl = (k+l)$ even, $(k$ and $l)$ both odd and both even
$h0l = l$ even
$hk0 = k$ even

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[a] Published by permission of the Director, Geological Survey.

[1] Richmond, W. E., *X*-ray crystallography of shortite: *Am. Mineral.* **26**, 288 (1941).

[2] *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Borntraeger, *Berlin* (1935).

$h00 = h$ all present
$0k0 = k$ even
$00l = l$ even

The four possible space groups compatible with these reflections are D_{2h}^{19}-$Ammm$, D_2^6-$A222$, C_{2v}^{11}-$A2mm$, C_{2v}^{14}-$Amm2$ or $Am2m$.

However, further consideration of the morphological development of the crystals, as given by Fahey,[3] shows that there is a vertical 2-fold axis of symmetry. The class symbol is therefore $mm2$. This conclusion together with the above reflections leads to the space group C_{2v}^{14}-$Amm2$.

An error in transcription appears in column 5, page 288. The number of atoms of O in the unit cell should be 18.00 in place of 18.3.

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[3] Fahey, J. J., Shortite, a new carbonate of sodium and calcium: *Am. Mineral.*, **24**, 515–516 (1939).

PROCEEDINGS OF SOCIETIES

CRYSTALLOGRAPHIC SOCIETY

The second meeting of the Crystallographic Society was held April 22, 1941, in the Mineralogical Lecture Room, Harvard University, Cambridge. Thirty-one members and guests were present. Professor M. J. Buerger, Acting President, spoke briefly of the purposes of the organization. The meeting was then addressed by Dr. I. Fankuchen on the topic "Preparation and Handling of Small Crystals." Instruments used in the growth and manipulation of micro-crystals and mounted micro-crystals of proteins were exhibited. In the ensuing discussion, special techniques used at the Massachusetts Institute of Technology and at Harvard University in handling minute crystals for *x*-ray and goniometric examination were described.

C. Frondel, *Acting Secretary*

PHILADELPHIA MINERALOGICAL SOCIETY

The Academy of Natural Sciences of Philadelphia, May 1, 1941

Dr. Thomas presided, with 69 members and visitors present. Mr. Harold D. Feuer addressed the society on "Buying Gem-stones in Foreign Markets." His reminiscences described experiences in Brazil and Ceylon.

Meeting of June 5, 1941

Dr. Thomas presided, with 60 members and visitors present. The evening was devoted to the commemoration of the Twenty-fifth Anniversary of the issue of the first number (July, 1916) of *The American Mineralogist.* The thought to establish this magazine was conceived by Samuel G. Gordon, then secretary of the Philadelphia Mineralogical Society, who had in mind a revival of the old *Mineral Collector* (1894–1909). To secure the support of amateur mineralogists an editorial board was set up of Wallace Goold Levison, secretary of the New York Mineralogical Club, Mr. W. Scott Lewis of the Mineral Collectors Association, and Dr. Edgar T. Wherry and Mr. Samuel G. Gordon of the Philadelphia Mineralogical Society. Dr. Levison was appointed editor, but the actual editorial work, as well as formulation of policy fell to Dr. Wherry, who became editor in title on the retirement of Dr. Levison in 1919. Mr. Robert Rosenbaum was the first business manager, but his studies prevented his continuing the work, and Mr. Harry W. Trudell assumed the position with the beginning of the second volume. Through circularization, an advance subscription fund was obtained, but loans to the magazine were made by Dr. Wherry, and Messrs. Trudell and Gordon. The actual work thus devolved upon these three: Dr. Wherry edited the magazine, Mr. Trudell handled all business affairs, and Mr. Gordon kept the stock, and mailed out the journal. However, generous money contributions from Col. Washington A. Roebling, Col. William Boyce Thompson, Mr. James G. Manchester, and George Vaux, Jr., erased the ever appearing deficit. By the end of the 4th volume, Mr. Trudell had brought it to the point where income not only balanced expenditures but with a cash balance of $381.82, in spite of the smallness of the number of subscriptions. With the organization of The Mineralogical Society of America, the magazine was taken over as its official journal with volume 5 in 1920.

Dr. Edgar T. Wherry described his early work in mineralogy, and the editorial policy of the magazine in its early days. Mr. R. B. Gage of Trenton, N. J., gave an account of the interest of Col. Washington A. Roebling in the magazine, and of his munificent endowment of it. The financial struggles were recalled by Mr. Harry W. Trudell. Mr. Gordon read a number of letters from the old files which recounted amusing experiences and letters received by the staff from subscribers, advertisers, and printers. Mr. Peter Zodac, Editor of a leading popular magazine on mineralogy, *Rocks and Minerals*, spoke on the present interest in collecting and of the support given by members of the society to his journal.

Mr. Lenker exhibited specimens of lapidary work of his students in the Radnor High School, and Mr. Hoffa exhibited some superb inlay work that he had made.

FORREST L. LENKER, *Secretary*

NEW DATA

Berlinite

H. STRUNZ: Isotypy von berlinite mit quartz. *Zeits. Krist.*, **103**, 228–229 (1941); through *Chem. Abstracts* **35**, 4315 (1941). Berlinite from Westanå, Sweden, was described by Blomstrand in 1868 as $4AlPO_4 \cdot H_2O$. Re-examination of type material confirms the validity of this mineral species and its identity with synthetic $AlPO_4$. *X*-ray study shows a hexagonal lattice with $a=4.92$, c 10.91Å., $c/a=2.217$; the unit cell contains $3(AlPO_4)$. The probable space group is $D_3^4-C3_12$ or $D_3^6-C3_22$. G.=2.64. Hardness 6–7. Optically uniaxial, positive, ω_{Na} 1.523, ϵ_{Na} 1.529.

MICHAEL FLEISCHER

Osbornite

F. A. BANNISTER: Osbornite, meteoritic titanium nitride. *Mineral. Mag.*, **26,** 36–44 (1941). Osbornite was described by Story-Maskelyne in 1870 as minute golden-yellow octahedra embedded in oldhamite (CaS) in the Bustee meteorite. Only 28 mg. was available, and from qualitative tests the mineral was believed to be an oxysulfide of Ca, Ti and/or Zr. *X*-ray study now shows osbornite to be face-centered cubic, with $a=4.235$Å. A fragment heated in the air to about 850° becomes polycrystalline and birefracting, and gives the *x*-ray pattern of rutile. Microchemical tests by M. H. Hey show the presence of Ti and the absence of Ca and S. These data indicate that osbornite is titanium nitride, TiN. Artificial TiN is face-centered cubic with $a=4.23$ Å, hardness 8–9, m.p. 3200°C., G. (calcd.)=5.39.

M. F.

DISCREDITED SPECIES

Stainierite, Mindigite, Trieuite (=Heterogenite)

V. Billiet and A. Vandendriessche: Les Oxydes hydrates de cobalt du Katanga. *Bull. Soc. Belge Geol.*, **49**, 63–78 (1939). *X*-ray powder pictures were made of stainerite from Kadjilangwe and Mindigi, of mindigite from Mindigi, of two samples of trieuite from the Belgian Congo, and of heterogenite from Goodsprings, Nevada. All gave the same *x*-ray pattern, differing only in that some gave weak pictures with only the strongest lines showing. An optically isotropic trieuite which gave a weak picture was recrystallized by heating in a sealed tube with water at 180°; the recrystallized material gave a sharp picture identical with those of other samples. The analyses in the literature are reviewed and the conclusion is reached that all can be represented by the formula $(Co_2O_3, CuO) \cdot H_2O$.

Discussion. The name heterogenite (Frenzel, 1872) has priority. The names stainierite (1929), mindigite (1934) and trieuite (1935) should be discarded. It seems probable that the following are also essentially heterogenite:—boodtite (*Mineral. Abs.*, **6**, 343 (1936), heubachite (also contains Ni, Dana's *System*, 6th Ed., p. 259), transvaalite (Dana's *System*, 6th Ed., p. 260), and schulzenite (Dana's *System*, 6th Ed., App. I, p. 61). It is noticeable that the samples which give the sharpest *x*-ray patterns give analyses close to $Co_2O_3 \cdot H_2O$, with little CuO and excess H_2O, whereas materials which are optically isotropic and give weak *x*-ray patterns contain much CuO and excess H_2O. It would seem, therefore, that the mineral should be regarded as $Co_2O_3 \cdot H_2O$ with adventitious CuO and H_2O.

M. F.